

Pending Claims of 09/961,735

1. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds and having an average particle diameter from about 5 nm to about 50 nm and a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.
2. The polishing composition of claim 1 wherein the particles are dispersed in an aqueous solution.
3. The polishing composition of claim 1 wherein the particles are dispersed in a nonaqueous solution.
4. The polishing composition of claim 1 wherein the particles comprise a composition selected from the group consisting of SiO_2 , SiC , TiO_2 , Fe_3C , Fe_7C_3 , Fe_2O_3 , Fe_3O_4 , MoS_2 , MoO_2 , WC , WO_3 , and WS_2 .
6. A method of smoothing a surface comprising the step of polishing the surface with the polishing composition of claim 1.
7. The method of claim 6 wherein the polishing is performed with a polishing pad.
8. The method of claim 6 wherein the polishing is performed with a motorized polisher.
9. The polishing composition of claim 1 having a single crystalline phase with a uniformity of at least about 90 percent by weight.
10. The polishing composition of claim 9 wherein the particles comprise a composition selected from the group consisting of SiO_2 , SiC , TiO_2 , Fe_3C , Fe_7C_3 , Fe_2O_3 , Fe_3O_4 , MoS_2 , MoO_2 , WC , WO_3 , and WS_2 .
12. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a uniformity of at least about 95 percent by weight.
13. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a purity of at least about 99 percent by weight.

14. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a purity of at least about 99.9 percent by weight.
15. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds or silicon compounds with an average particle diameter from about 5 nm to about 50 nm and effectively no particles with a diameter greater than about 5 times the average diameter.
16. A polishing composition comprising an aqueous dispersion of particles, the particles comprising metal carbides or metal sulfides and having an average particle diameter from about 5 nm to about 200 nm.
23. The polishing composition of claim 15 wherein the particles are dispersed in an aqueous solution.
25. The polishing composition of claim 16 wherein the particles have an average diameter from about 5 nm to about 100 nm.
26. The polishing composition of claim 16 wherein the dispersion includes from about 0.05 to about 5 percent by weight particles.



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United States Patent [19]

Neville et al.

[11] Patent Number: **5,527,423**[45] Date of Patent: **Jun. 18, 1996**[54] **CHEMICAL MECHANICAL POLISHING
SLURRY FOR METAL LAYERS**

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[51] Int. Cl.⁶ **B24B 1/00; H01L 21/00**

[52] U.S. Cl. **156/636.1; 252/79.1; 51/308; 106/3**

[58] Field of Search **156/636.1, 645.1, 156/656.1; 252/79.1, 79.5; 51/308; 106/3**

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Primary Examiner—Thi Dang

[57] **ABSTRACT**

A slurry for use in chemical-mechanical polishing of a metal layer comprising high purity fine metal oxide particles uniformly dispersed in a stable aqueous medium.

39 Claims, 8 Drawing Sheets

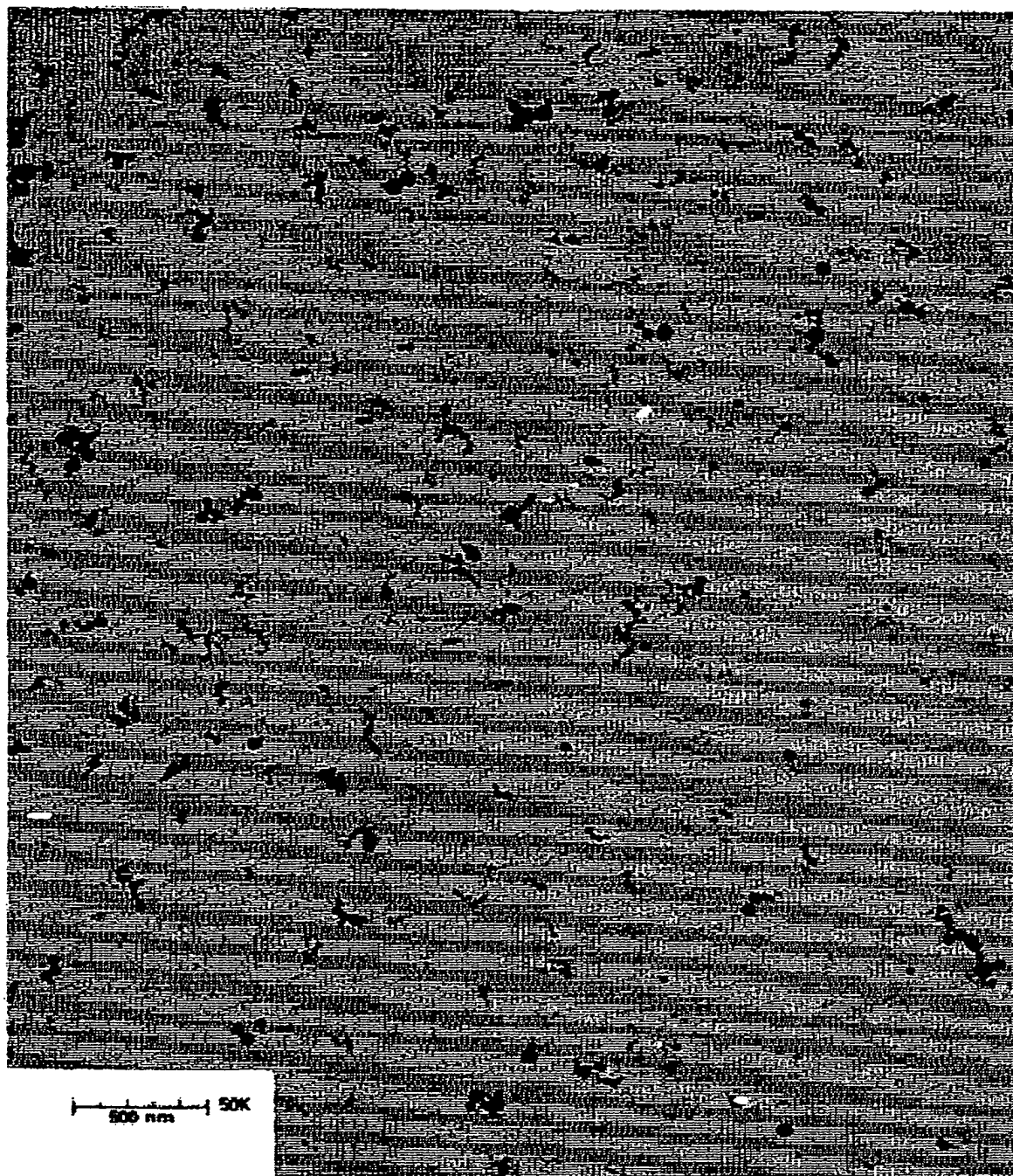


FIG. 1

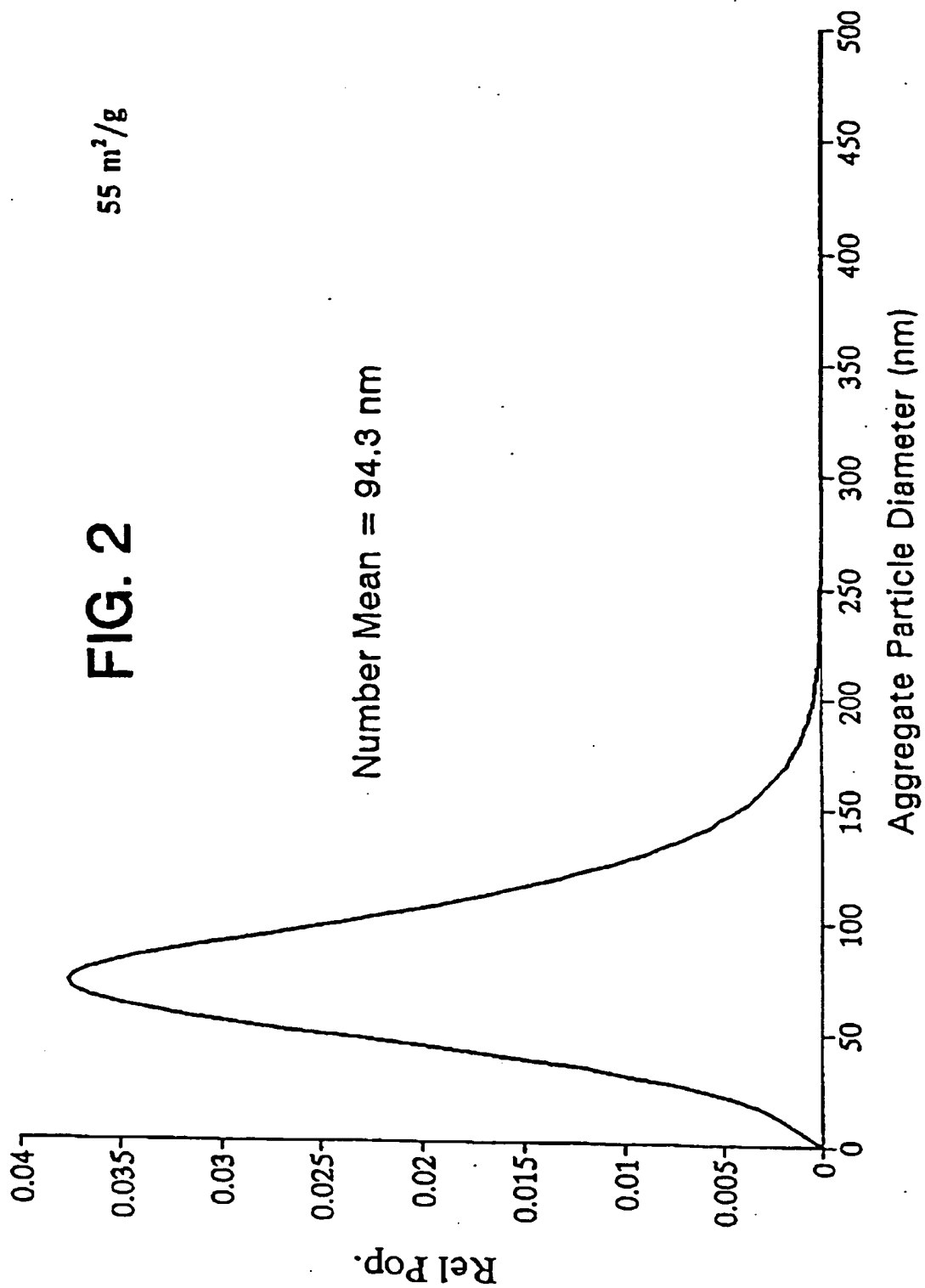


FIG. 3

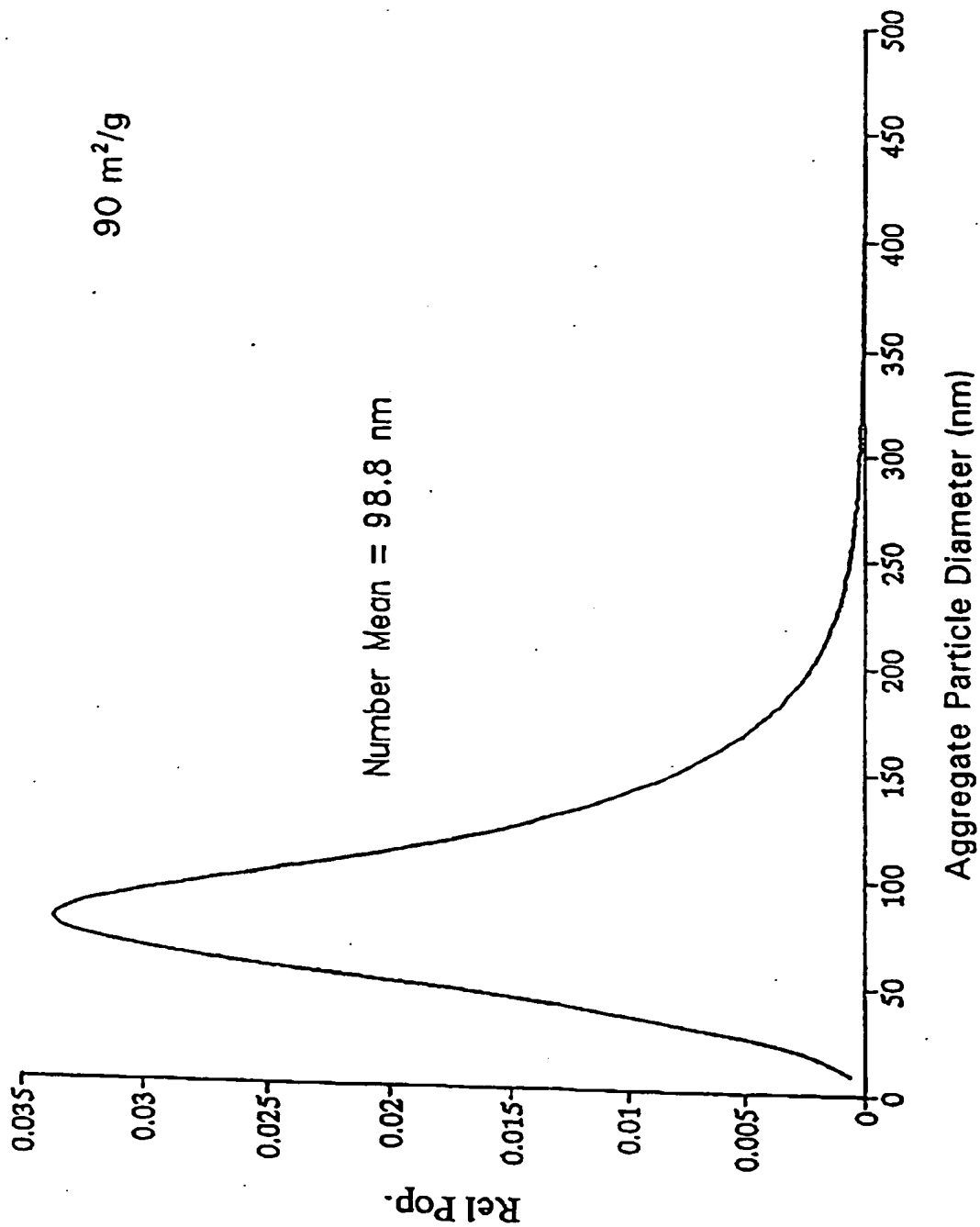


FIG. 4

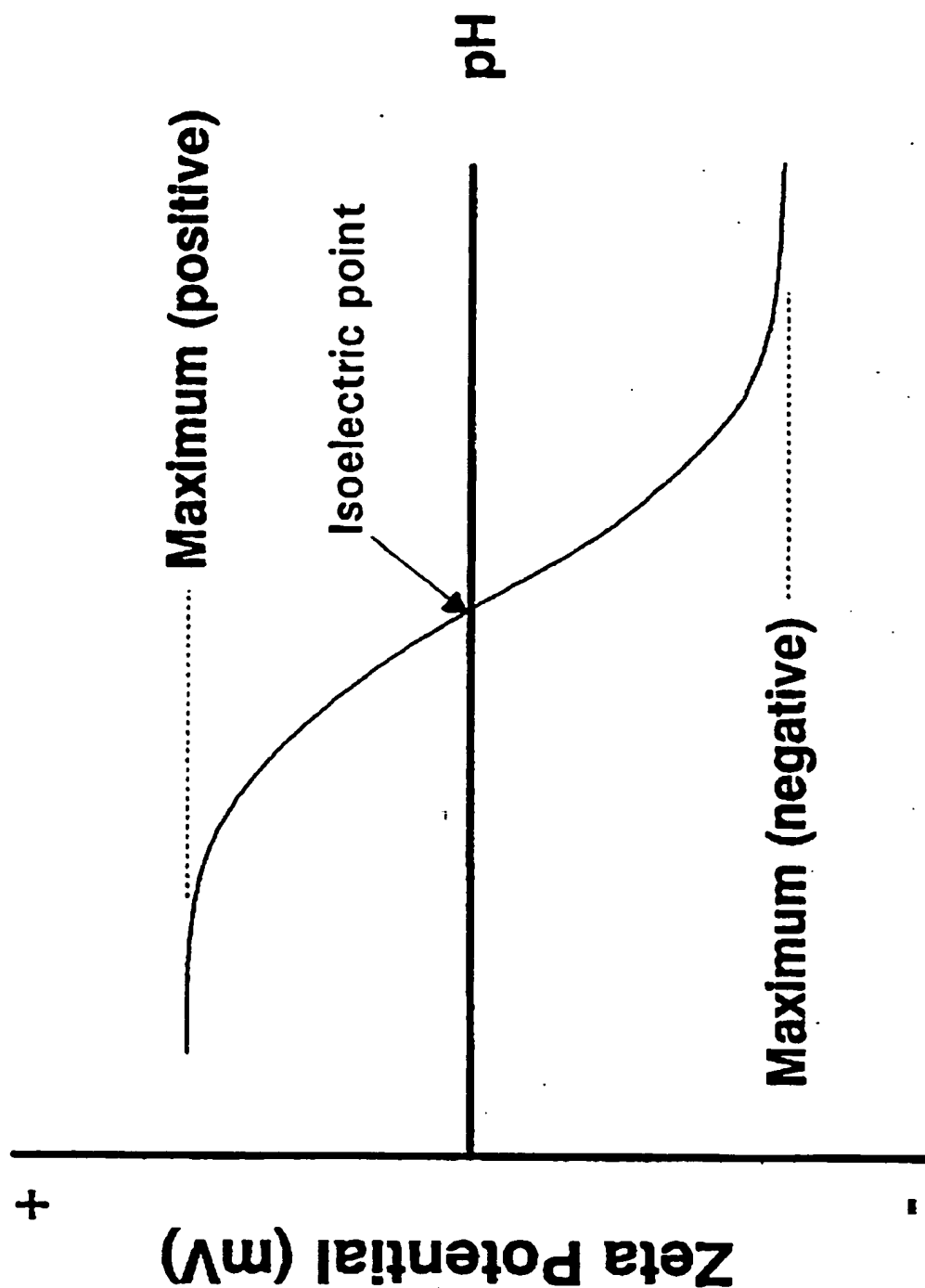


FIG. 5

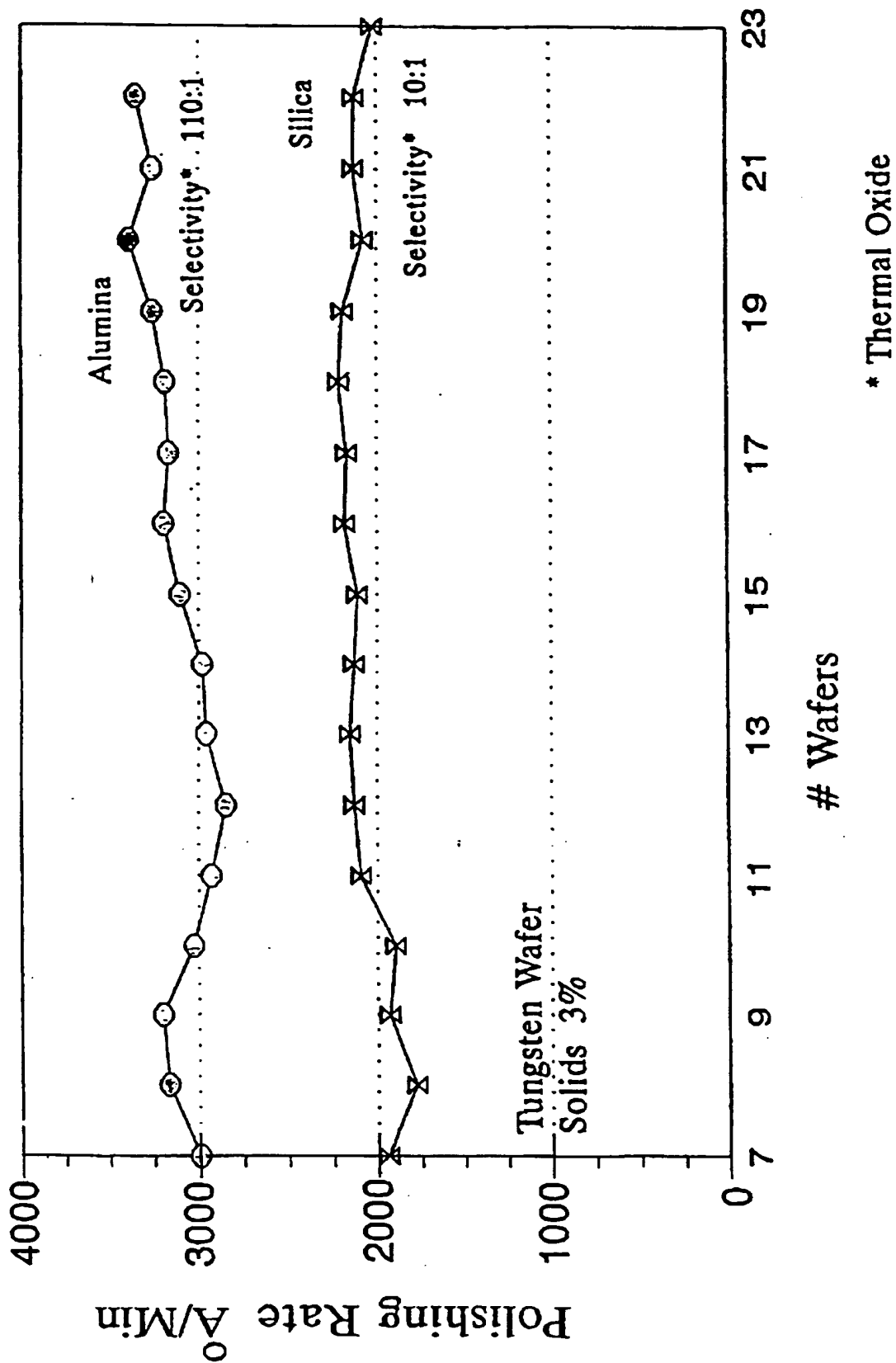
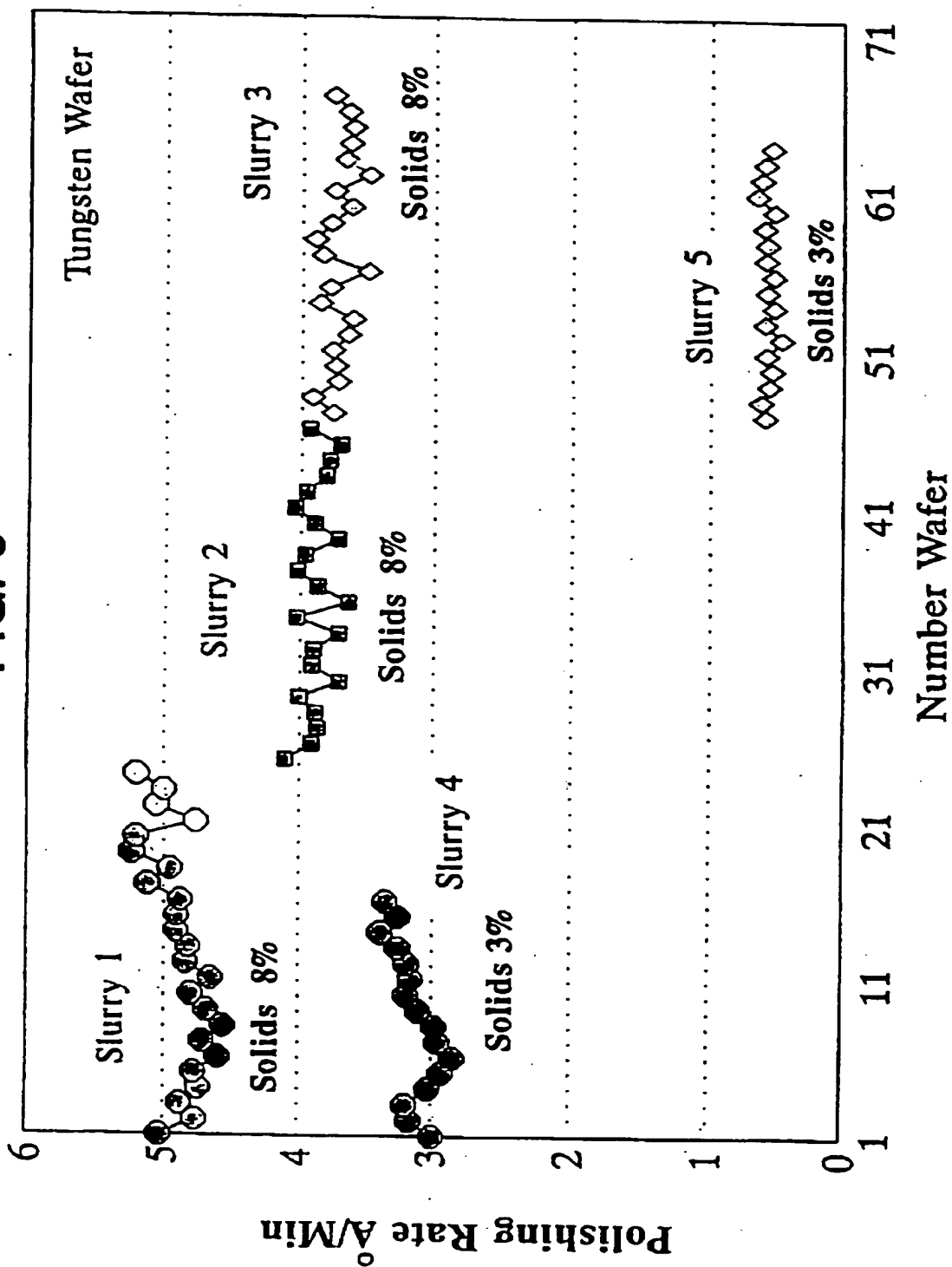


FIG. 6



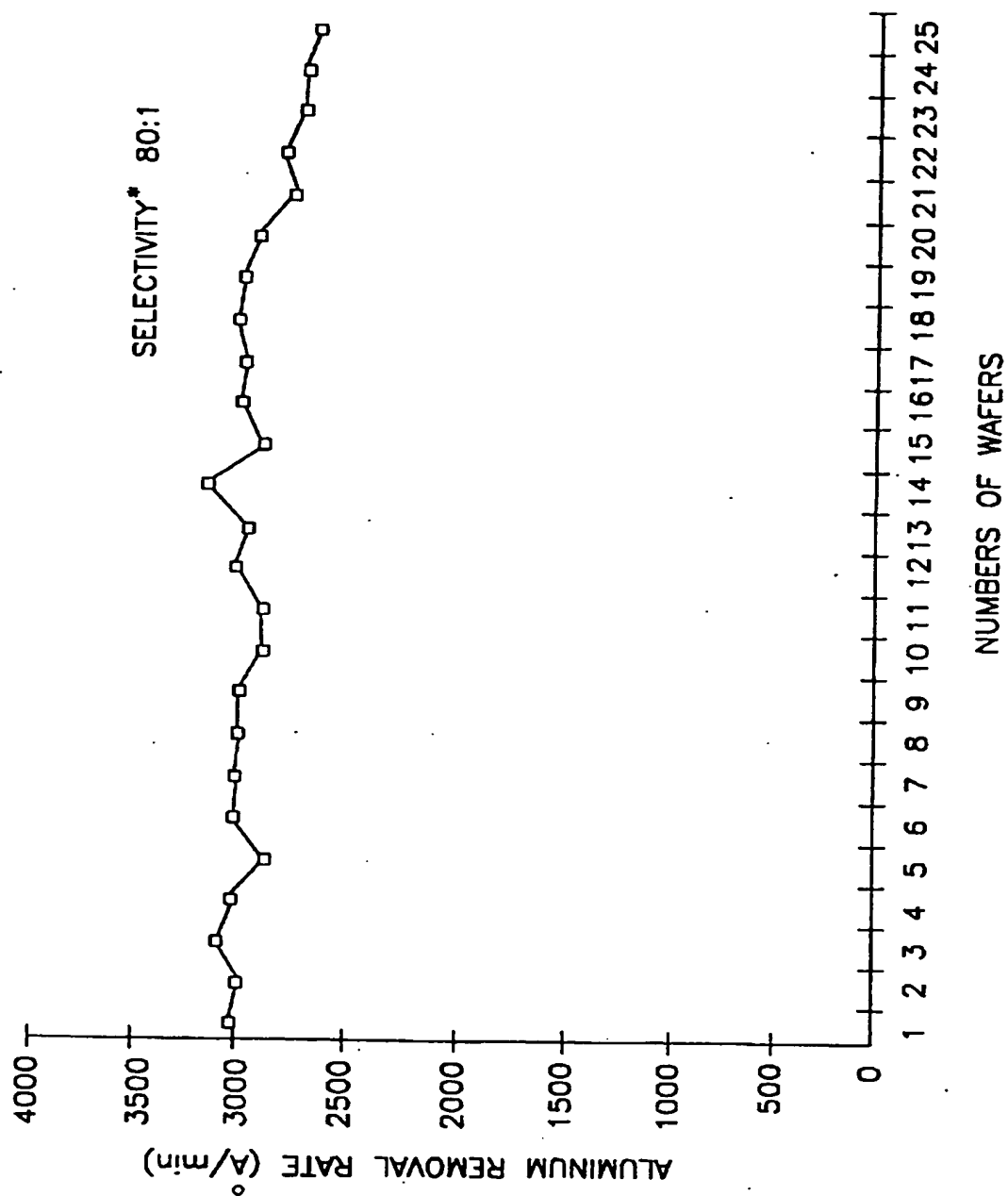


FIG. 7

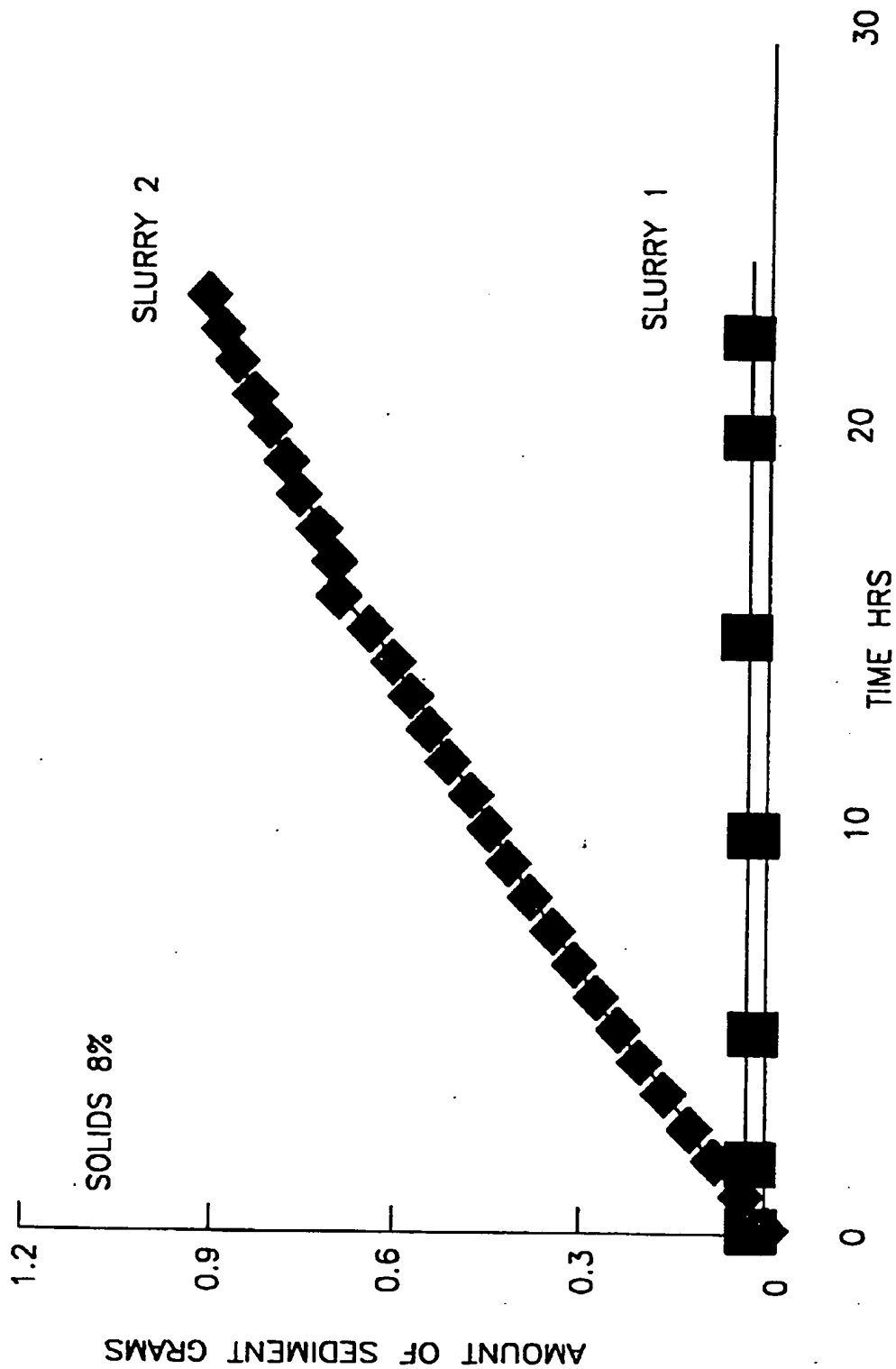


FIG. 8

CHEMICAL MECHANICAL POLISHING SLURRY FOR METAL LAYERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a chemical mechanical polishing slurry for semiconductor device planarization and, more particularly, to a chemical mechanical polishing slurry for use on polishing metal layers.

2. Background of the Invention

A semiconductor wafer typically includes a substrate, such as such as a silicon or gallium arsenide wafer, on which a plurality of integrated circuits have been formed. Integrated circuits are chemically and physically integrated into a substrate by patterning regions in the substrate and layers on the substrate. The layers are generally formed of various materials having either a conductive, insulating or semiconducting nature. In order for a device to have high yields, it is crucial to start with a flat semiconductor wafer and, as a result, it is often necessary to polish a side or part of a semiconductor wafer. If the process steps of device fabrication are performed on a wafer surface that is not uniform, various problems can occur which may result in a large number of inoperable devices. For example, in fabricating modern semiconductor integrated circuits, it is necessary to form conductive lines or similar structures above a previously formed structure. However, prior surface formation often leaves the top surface topography of a wafer highly irregular, with bumps, areas of unequal elevation, troughs, trenches and other similar types of surface irregularities. As a result, global planarization of such surfaces is necessary to ensure adequate focus depth during photolithography, as well as removing any irregularities and surface imperfections during the various stages of the fabrication process. Although several polishing techniques exist to ensure wafer surface planarity, processes employing chemical mechanical planarization or polishing techniques have achieved widespread usage to planarize the surface of wafers during the various stages of device fabrication in order to improve yield, performance and reliability. In general, chemical mechanical polishing ("CMP") involves the circular motion of a wafer under a controlled downward pressure with a polishing pad saturated with a conventional polishing slurry. For a more detailed explanation of chemical mechanical polishing, please see U.S. Pat. Nos. 4,671,851, 4,910,155 and 4,944,836, the specifications of which are incorporated herein by reference.

Typical polishing slurries available for CMP oxide processes contain an abrasive material such as silica or alumina in an acidic or basic solution. For example, U.S. Pat. No. 5,245,790 to Jerbic describes a technique for chemical mechanical polishing of semiconductor wafers using ultrasonic energy and a silica based slurry in a KOH solution. U.S. Pat. No. 5,244,534 to Yu et al. discloses a method of forming conductive plugs within an insulation layer. The process results in a plug of material, such as tungsten, which is more even with the insulation layer surface than that achieved using conventional plug formation techniques. Slurries of abrasive particles such as Al_2O_3 and etchants such as H_2O_2 and either KOH or NH_4OH are used in the first CMP step to remove the tungsten at a predictable rate while removing very little of the insulation. The second CMP step utilizes a slurry consisting of an abrasive material, such as aluminum oxide, and an oxidizing component of hydrogen peroxide and water. Similarly, U.S. Pat. No. 5,209,816 to Yu

et al. teaches a CMP slurry comprising H_3PO_4 , H_2O_2 , H_2O and a solid abrasive material while U.S. Pat. Nos. 5,157,876 and 5,137,544 to Medellin teach stress free CMP agents for polishing semiconductor wafers which include a mixture of water, colloidal silica and bleach containing sodium hypochlorite. U.S. Pat. No. 4,956,313 to Cote et al. discloses a slurry consisting of Al_2O_3 particulates, deionized water, a base and an oxidizing agent.

Since CMP has been successfully used to polish oxide surfaces for a number of years, a recent trend in the semiconductor industry is to utilize CMP techniques and slurries for polishing metal layers. However, even though some slurries and polishing techniques have been directed to metal layers, films and plugs, such as tungsten, aluminum and copper, chemical mechanical polishing of these metals for device fabrication has not been well understood or developed. As a result, the use of conventional silica or alumina slurries on metal layers has resulted in unacceptable polishing performance and yielded devices of poor quality. Accordingly, a need remains for improved chemical mechanical polishing techniques and slurries for the same which provide uniform metal layers, free from undesirable contaminants and surface imperfections.

SUMMARY OF THE INVENTION

The present invention is directed to a chemical mechanical polishing slurry for polishing metal layers of semiconductor devices comprising high purity, fine metal oxide particles uniformly dispersed in a stable aqueous medium. The particles have a surface area ranging from about 40 m^2/g to about 430 m^2/g , an aggregate size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between the particles. In a preferred embodiment, the metal oxide particles also have a maximum zeta potential greater than about ± 10 millivolts. Also disclosed is a method of polishing tungsten layers with the polishing slurry of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a transmission electron micrograph (TEM) showing metal oxide particles of fumed alumina of the present invention at 50,000x magnification.

FIG. 2 is an aggregate size distribution for metal oxide particles of fumed alumina for use in the polishing slurry of the present invention.

FIG. 3 is an aggregate size distribution for metal oxide particles of fumed silica for use in the polishing slurry of the present invention.

FIG. 4 illustrates a theoretical plot of pH on the x-axis versus zeta potential in millivolts on the y-axis.

FIG. 5 illustrates the effect of the particle composition on tungsten polishing rate and selectivity to thermal oxide for a series of wafers utilizing the polishing slurry of the present invention. The x-axis indicates the wafer number and the y-axis indicates the polishing rate of tungsten in $\text{\AA}/\text{minute}$.

FIG. 6 illustrates the effect on particle morphology, phase and solids content on tungsten polishing rate for a series of wafers utilizing the polishing slurry of the present invention. The x-axis indicates the wafer number and the y-axis indicates the polishing rate of tungsten in $\text{\AA}/\text{minute}$.

FIG. 7 illustrates the polishing rate of aluminum and selectivity to thermal oxide for a series of wafers utilizing the polishing slurry of the present invention. The x-axis

indicates the wafer number and the y-axis indicates the polishing rate of aluminum in Å/minute.

FIG. 8 illustrates the influence that aggregate size distribution and zeta potential has on colloidal stability by plotting the amount of sediment as a function of time.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a chemical mechanical polishing slurry comprising high purity, fine metal oxide particles uniformly dispersed in an aqueous medium. The particles of the present invention differ from the "abrasive particles" of the prior art by having a surface area ranging from about 40 m²/g to about 430 m²/g, an aggregate size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between the particles. By way of illustration, FIG. 1 is a TEM (transmission electron micrograph) for metal oxide particles of fumed alumina in the slurry of the present invention.

The surface area of the particles, as measured by the nitrogen adsorption method of S. Brunauer, P. H. Emmet, and L. Teller, J. Am. Chemical Society, Volume 60, Page 309 (1938) and commonly referred to as BET, typically ranges from about 40 m²/g to about 430 m²/g. The particles may comprise between 0.5% and 55% of the slurry depending on the degree of abrasion required. The abrasion of the metal oxide particles, in turn, is a function of the particle composition, the degree of crystallinity and the crystalline phase, e.g. gamma or alpha for alumina. In order to achieve the desired selectivity and polishing rate, it has been found that the optimum surface area and loading level will vary depending upon which fine metal oxide particles are chosen for a particular polishing slurry, as well as the degree of crystallinity and phase of the particles. In one embodiment when a high degree of selectivity is desired, solid loadings of less than 12% by weight for alumina particles having surface areas ranging from about 70 m²/g to about 170 m²/g is preferred. At lower surface areas, i.e. less than 70 m²/g, solid loadings of less than 7% is preferred for alumina particles. Similarly when a low selectivity is desired, it has been discovered that when the fine metal oxide particle is fumed silica, surface areas ranging between 40 m²/g and 250 m²/g should be present in a range from about 0.5% to about 20% by weight.

The metal oxide particles of the present invention are of a high purity and have an aggregate size distribution of less than about 1.0 micron in order to avoid scratching, pit marks, divots and other surface imperfections during the polishing. By way of example, FIGS. 2 and 3 illustrate aggregate size distributions for metal oxide particles of the present invention for fumed alumina and silica, respectively. High purity means that the total impurity content is typically less than 1% and preferably less than 0.01% (i.e. 100 ppm). Sources of impurities typically include raw material impurities and trace processing contaminants. The aggregate size of the particles refers to the measurement of the branched, three dimensional chains of fused primary particles (individual molten spheres). It should be noted that although it is common to refer to the terms "particle," "primary particle" and "aggregate particle" interchangeably, such reference is inaccurate and misleading. For example, what is typically meant by the term "particle size" is in fact the average maximum dimension of the "aggregate particle or aggregates" and not the "primary particles." Therefore, careful

appreciation and differentiation of aggregates and primary particles is essential to those skilled in the art.

One method of determining the aggregate size distribution in the present invention was by transmission electron microscopy (TEM). In this method, the metal oxide particle sample is dispersed in a liquid medium until the agglomerates have been reversed to aggregates. Its concentration is then adjusted until discrete aggregates are shown on the TEM grid. Multiple fields on the grid are then imaged using an image analysis system manufactured by Kontron Instruments (Everett, Mass.) and stored on a video tape until greater than 1000 aggregates are imaged and stored. The stored images are in turn fed into an image analysis computer with a frame-grabber board for further processing, i.e. cleaning up aberrations, adjusting background and normalizing the image. Individual aggregates in the binary field are measured for a number of particle parameters, i.e. aggregate size, using known techniques such as that described in ASTM D3849-89. Measurements may be recalled individually or in the form of statistical or histogram distributions.

In order for the polishing slurry of the present invention to be an effective alternative to conventional slurries, it is important that the aggregates of the metal oxide particles are uniformly dispersed in a stable aqueous medium. By uniformly dispersed is meant that the aggregates are isolated and well distributed throughout the medium. By stable is typically meant that the aggregates will not re-agglomerate and settle out (e.g. form a hard, dense sediment). In a preferred embodiment, the aggregates will remain stable for at least a three month period of time. Critical to achieving slurry stability, it has been further discovered that the metal oxide particles of the present invention, in addition to having an aggregate size distribution less than 1.0 micron, have an average or mean aggregate diameter of less than about 0.4 micron and that the particles of the present invention have a force sufficient to repel and overcome the van der Waals attractive forces between the particles. The mean aggregate diameter refers to the average equivalent spherical diameter when using TEM image analysis, i.e. based on the cross-sectional area of the aggregate. By force is meant that either the surface potential or the hydration force of the metal oxide particles must be sufficient to repel and overcome the van der Waals attractive forces between the particles.

In a preferred embodiment, the metal oxide particles will have a mean aggregate size distribution less than 0.3 micron and also have a maximum zeta potential greater than ±10 millivolts. Zeta potential (ζ) is the potential difference, measured in a liquid, between the shear plane and the bulk of the liquid beyond the limits of the electrical double layer. The zeta potential is dependent on the pH of the aqueous medium as illustrated in FIG. 4. For a given metal oxide particle composition, the isoelectric point is defined as the pH at which zeta potential is zero. As the pH is increased or decreased away from the isoelectric point, the surface charge is increased negatively or positively, respectively. As the pH continues to increase or decrease, the surface charge will reach an asymptote, the asymptote being referred to as the maximum zeta potential. It should be noted that the maximum zeta potential and isoelectric point are functions of the metal oxide composition and that the maximum zeta potential can be effected by the addition of salts to the aqueous medium. For a more complete discussion of zeta potentials, please see R. J. Hunter, *Zeta Potential in Colloid Science* (Academic Press 1981).

Although zeta potential cannot be measured directly, the zeta potential can be measured by a variety of known

techniques, such as electrophoresis, electrokinetic sonic amplitude, and analytical techniques including ultrasonic vibration potential. In the present invention, the zeta potential referred to was determined by measurement of the electrokinetic sonic amplitude using the Matec MBS-8000 instrument (available from Matec Applied Sciences, Inc., Hopkington, Mass.).

In another embodiment, an oxidizing component may be added to the polishing slurry to oxidize the metal layer to its corresponding oxide. For example, in the present invention, an oxidizing component is used to oxidize a metal layer to its corresponding oxide, such as tungsten to tungsten oxide. The layer is mechanically polished to remove the tungsten oxide from the layer. Although a wide range of oxidizing components may be used, preferred components include oxidizing metal salts, oxidizing metal complexes, iron salts such as nitrates, sulfates, EDTA, citrates, potassium ferricyanide and the like, aluminum salts, sodium salts, potassium salts, ammonium salts, quaternary ammonium salts, phosphonium salts, peroxides, chlorates, perchlorates, permanganates, persulfates and mixtures thereof. Typically, the oxidizing component is present in the slurry in an amount sufficient to ensure rapid oxidation of the metal layer while balancing the mechanical and chemical polishing components of the slurry. In addition, it has further been discovered that a critical relationship exists between the concentration of the oxidizing component and the colloidal stability of the polishing slurry. As such, oxidizing components are typically present in the slurry from about 0.5% to 15% by weight, and preferably in a range between 1% and 7% by weight.

In order to further stabilize a polishing slurry containing an oxidizing component against settling, flocculation and decomposition of the oxidizing component, a variety of additives, such as surfactants, polymeric stabilizers or other surface active dispersing agents, can be used. Many examples of suitable surfactants for use in the present invention are disclosed in, for example, Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 22 (John Wiley & Sons, 1983); Sislet & Wood, *Encyclopedia of Surface Active Agents* (Chemical Publishing Co., Inc., 1964) and available manufacturing literature, including for example McCutcheon's *Emulsifiers & Detergents*, North American and International Edition (McCutcheon Division, The MC Publishing Co., 1991); Ash, *The Condensed Encyclopedia of Surfactants* (Chemical Publishing Co., Inc. 1989); Ash, *What Every Chemical Technologist Wants to Know About . . . Emulsifiers and Wetting Agents, Volume I* (Chemical Publishing Co., Inc. 1988); Tadros, *Surfactants* (Academic Press, 1984); Napper, *Polymeric Stabilization of Colloidal Dispersion* (Academic Press, 1983); and Rosen, *Surfactants & Interfacial Phenomena*, 2nd edition (John Wiley & Sons, 1989), all of which are incorporated herein by reference. In one embodiment, a surfactant consisting of a copolymer of polydimethyl siloxane and polyoxyalkylene ether was found to be suitable.

In general, the amount of an additive used, such as a surfactant, in the present invention should be sufficient to achieve effective steric stabilization of the slurry and will typically vary depending on the particular surfactant selected and the nature of the surface of the metal oxide particle. For example, if not enough of a selected surfactant is used, it will have little or no effect on stabilization. On the other hand, too much of the surfactant may result in undesirable foaming and/or flocculation in the slurry. As a result, additives like surfactants should generally be present in a range between about 0.001% and 10% by weight. Further-

more, the additive may be added directly to the slurry or treated onto the surface of the metal oxide particle utilizing known techniques. In either case, the amount of additive is adjusted to achieve the desired concentration in the polishing slurry.

The metal oxide particles of the present invention are typically precipitated aluminas, fumed silicas or fumed aluminas and preferably are fumed silicas or fumed aluminas. The production of fumed silicas and aluminas is a well-documented process which involves the hydrolysis of suitable feedstock vapor, such as silicon tetrachloride or aluminum chloride, in a flame of hydrogen and oxygen. Molten particles of roughly spherical shapes are formed in the combustion process, the diameters of which are varied through process parameters. These molten spheres of fumed silica or alumina, typically referred to as primary particles, fuse with one another by undergoing collisions at their contact points to form branched, three dimensional chain-like aggregates. The force necessary to break aggregates is considerable and often considered irreversible. During cooling and collecting, the aggregates undergo further collision that may result in some mechanical entanglement to form agglomerates. Agglomerates are thought to be loosely held together by van der Waals forces and can be reversed, i.e. de-agglomerated, by proper dispersion in suitable media.

The precipitated metal oxide particles may be manufactured utilizing conventional techniques and are typically formed by the coagulation of the desired particles from an aqueous medium under the influence of high salt concentrations, acids or other coagulants. The particles are filtered, washed, dried and separated from residues of other reaction products by conventional techniques known to those skilled in the art.

Once produced, the metal oxide is slowly added to deionized water to form a colloidal dispersion. The slurry is completed by subjecting the dispersion to high shear mixing using conventional techniques. The pH of the slurry is adjusted away from the isoelectric point to maximize colloidal stability. The polishing slurry of the present invention may be used as a one package system (metal oxide particles and oxidizing component, if desired, in a stable aqueous medium) or two package system (the first package consists of the metal oxide particles in a stable aqueous medium and the second package consists of oxidizing component) with any standard polishing equipment appropriate for use on the desired metal layer of the wafer. The two package system is used when an oxidizing component decomposes or hydrolyzes in the presence of certain metal oxide particles over time. In the two package system, the oxidizing component may be added to the slurry just prior to polishing.

The polishing slurry of the present invention has been found useful in providing effective polishing to metal layers at desired polishing rates while minimizing surface imperfections and defects. Non-limiting illustrations of the polishing slurry of the present invention follow.

EXAMPLE 1

Two polishing slurries were prepared. The first slurry consisted of 3 weight percent fumed alumina, 5 weight percent ferric nitrate and the remainder deionized water. The second slurry consisted of 3 weight percent fumed silica, 5 weight percent ferric nitrate and the remainder deionized water. Further properties of both slurries are described in Table I. The two slurries were utilized to chemically-mechanically polish a tungsten layer having a thickness of

approximately 7500 Å. The polishing conditions and performance results are illustrated in Table II.

TABLE I

Slurry Base	Surface Area (m ² /g)	Aggregate Diameter (nm)	Max. Zeta Potential (mV)	Phase
Fumed Alumina	55	86	>+30	80% gamma
Fumed Silica	90	109	>+12	Amorphous

TABLE II

Slurry Base	Pressure (psi)	Flow Rate (ml/min)	Table Speed (rpm)	Spindle Speed (rpm)	Polishing (Å/min)	Selectivity*	Quality†
Fumed Alumina	5	200	50	50	3000	110:1	High
Fumed Silica	5	200	50	50	2000	10:1	High

(*Thermal Oxide; †High = Less than 10 defects/wafer)

As can be seen from Table II, and further illustrated in FIG. 5, both polishing slurries of the present invention were effective in achieving acceptable polishing rates and wafer surfaces of a high quality. Moreover, it can be seen that the composition of the metal oxide particle and its phase have an impact on the polishing rate of the tungsten layer and on selectivity (i.e. the polishing rate ratio between tungsten and thermal oxide). As a result, the particular metal oxide chosen for polishing a layer of tungsten may depend on the desired selectivity and polishing rate.

EXAMPLE 2

For comparative purposes, a conventional slurry was prepared consisting of 8 weight percent of a commercial alumina, 5 weight percent ferric nitrate and the remainder deionized water. The slurry was utilized to chemically mechanically polish a tungsten layer having a thickness of approximately 7500 Å. Under similar polishing conditions to that used in Example 1, the slurry of commercial alumina removed 750 Å/min and produced wafers of a poor quality.

percent fumed alumina, 5 weight percent ferric nitrate and the remainder deionized water, were prepared to examine the effect of particle morphology and crystallinity under aggressive polishing conditions, i.e. high pressure, high table speed, high solids loading. The fourth and fifth slurries, which consisted of 3 weight percent fumed alumina, 5 weight percent ferric nitrate and the remainder deionized water, were prepared to examine the effect of particle morphology and crystallinity under less aggressive polishing conditions, i.e. low pressure, low table speed and low solids loading. Further properties of the slurries are described in Table III. The five slurries were utilized to chemically-mechanically polish a tungsten layer having a

thickness of approximately 7500 Å. The polishing conditions and performance results are illustrated in Table IV.

TABLE III

Slurry	Surface Area (m ² /g)	Aggregate Diameter (nm)	Max. Zeta Potential (mV)	Phase
1	55	86	+20-35	80% gamma
2	85	88	>+30	40% gamma
3	100	87	>+20	20% gamma
4	55	86	>+30	80% gamma
5	100	87	>+20	20% gamma

TABLE IV

Slurry	Pressure (psi)	Flow Rate (ml/min)	Table Speed (rpm)	Spindle Speed (rpm)	Polishing (Å/min)	Selectivity*	Quality†
1	9	200	100	25	4850	50:1	Low
2	9	200	100	25	3900	110:1	Low
3	9	200	100	25	3700	NA	High
4	6	200	50	50	3100	NA	High
5	6	200	50	50	600	NA	High

(*Thermal Oxide; †High = Less than 10 defects/wafer; Low = Greater than 100 defect/wafer.)

The polishing rate obtained by the slurry of commercial alumina was unacceptable for most polishing applications.

EXAMPLE 3

Five polishing slurries were prepared to investigate the effect of particle morphology and solids content on the polishing performance for a fumed alumina slurry. The first, second and third slurries, which consisted of 8 weight

Under the aggressive polishing conditions of slurries 1-3, the phase and morphology, i. e. surface area, of the fumed alumina particles have been found to have a significant effect on selectivity (i.e. the polishing rate ratio between tungsten and thermal oxide) and surface quality and a less dramatic effect on polishing rate, as illustrated in Table IV and further represented in FIG. 6. Under the less aggressive conditions of slurries 4 and 5, the phase and morphology have a significant effect on polishing rate and surface quality. For

example, high quality wafers were produced by polishing with slurries 3 (at 8% loading), 4 (at 3% loading) and 5 (at 3% loading). However, a higher solids loading level was needed for the high surface area aluminas in order to also achieve a suitable polishing rate. On the other hand, slurries 1 (at 8% loading) and 2 (at 8% loading), although achieving very high polishing rates, produced wafers with low surface quality. Although not completely understood, it has therefore important to recognize, as demonstrated herein, that the inter-relationship between the composition of the slurry and morphology of the fine metal oxide particles (i.e. surface area, aggregate size and diameter, degree of crystallinity, crystalline phase) is critical to achieving an effective polishing slurry.

EXAMPLE 4

A polishing slurry was prepared consisting of 8 percent fumed silica, 5 weight percent ferric nitrate and the remainder deionized water. Further properties of the slurry are described in Table V. The slurry was utilized to chemically-mechanically polish an aluminum layer having a thickness of approximately 7500 Å. The polishing conditions and performance results are illustrated in Table VI.

TABLE V

Particle Comp.	Surface Area (m ² /g)	Aggregate Diameter (nm)	Max. Zeta Potential (mV)	Phase
Fumed Silica	90	109	-412	Amorphous

TABLE VI

Slurry	Pressure (psi)	Flow Rate (ml/min)	Table Speed (rpm)	Spindle Speed (rpm)	Polishing (Å/min)	Selectivity*	Quality†
Fumed Silica	9	200	50	25	2932	80:1	High

(*Thermal Oxide; †High = Less than 10 defects/wafer)

As shown in Table VI and further illustrated in FIG. 7, the polishing slurry of the present invention is effective in achieving an acceptable polishing rate for an aluminum layer and wafers with high surface quality.

EXAMPLE 5

Two slurries were prepared to illustrate the effect of aggregate size distribution and maximum zeta potential on colloidal stability. The first slurry consisted of 8 weight percent fumed alumina as described in the present invention, 5 weight percent ferric nitrate and the remainder deionized water. The second slurry consisted of 8 weight percent of a commercially available precipitated alumina sold under the name Ultralox M100. Further properties of the slurries are listed in Table VII.

TABLE VII

Slurry	Surface Area (m ² /g)	Mean Aggregate Diameter (nm)	Max. Zeta Potential (mV)
1	55	94.3	+32
2	NA	450	+10

FIG. 8 illustrates the amount of metal oxide particles in the respective slurries which settled over a twenty-four hour period. The particles were measured using a Dynometer instrument manufactured by Byk Gardner, Inc. As noted, no settling was detected in slurry 1 of the present invention. On the other hand, slurry 2 of commercially available alumina showed a continuous build-up in sediment over the twenty-four hour period. At the end of the period, the bulk of the alumina had settled out to form a dense hard cake. When used at this time without additional steps to redisperse the cake and stabilize the slurry, slurry 2 achieved low polishing rates and produced significant scratching on the wafer, thus yielding a wafer of poor quality.

As described herein, the polishing slurry of the present invention has been found particularly useful in chemical mechanical planarization to remove uneven topography, layers of material, surface defects including scratches, roughness, or contaminant particles such as dirt or dust. As a result, semiconductor processes utilizing this slurry experience an improvement in surface quality, device reliability and yield as compared to conventional etch back techniques. Although the fine metal oxide particles have been directed to aluminas and silicas, it is understood that the teachings herein have applicability to other fine metal oxide particles such as germania, ceria, titania and the like. Furthermore, the metal oxide particles may be utilized to polish other metal surfaces such as copper and titanium, as well as underlayers such as titanium, titanium nitride and titanium tungsten.

It is further understood that the present invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be

made without departing from the scope and spirit of the invention.

What is claimed is:

1. A method for chemical-mechanical polishing a metal layer of a substrate, the method which comprises the steps of:
 - a) providing a chemical mechanical polishing slurry comprising high purity, alumina particles uniformly dispersed in an aqueous medium having a surface area ranging from about 40 m²/g to about 430 m²/g, an aggregate size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between the particles, wherein said slurry is stable; and
 - b) chemical mechanical polishing a metal layer on a semiconductor substrate with said slurry.
2. The method of claim 1 wherein said metal layer is selected from the group consisting of: tungsten, aluminum, copper, titanium, and alloys thereof.
3. The method of claim 2 wherein said metal layer is tungsten.
4. The method of claim 3 wherein said tungsten layer further comprising at least one underlayer selected from the

group consisting of: titanium, titanium nitride and titanium tungsten and mixtures thereof.

5. The method of claim 1 wherein said particles are present in a range between about 0.5% and 55% by weight.

6. The method of claim 1 wherein said alumina particles have a surface area less than about 70 m²/g and are present in said slurry in a range less than about 7% by weight.

7. The method of claim 1 wherein said alumina particles have a surface area ranging between about 70 m²/g to about 170 m²/g and are present within said slurry in a range less than about 12% by weight.

8. The method of claims 6 or 7 wherein said alumina is a precipitated alumina or a fumed alumina.

9. The method of claim 1 wherein said particles have a maximum zeta potential greater than about ± 10 millivolts.

10. The method of claim 1 wherein said slurry further comprises an oxidizing component.

11. The method of claim 10 wherein said oxidizing component is an oxidizing metal salt.

12. The method of claim 10 wherein said oxidizing component is an oxidizing metal complex.

13. The method of claim 10 wherein said oxidizing component is selected from the group consisting of: iron salts, aluminum salts, sodium salts, potassium salts, ammonium salts, quaternary ammonium salts, phosphonium salts, peroxides, chlorates, perchlorates, permanganates, persulfates and mixtures thereof.

14. The method of claim 1 wherein said slurry further comprises a surfactant.

15. The method of claim 14 wherein the surfactant is selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants and mixtures thereof.

16. The method of claim 14 wherein said surfactant is selected from the group consisting of: polyalkyl siloxanes, polyaryl siloxanes, polyoxyalkylene ethers, and mixtures and copolymers thereof.

17. A chemical-mechanical polishing slurry for polishing a metal layer comprising:

high purity, alumina particles uniformly dispersed in an aqueous medium having a surface area ranging from about 40 m²/g to about 430 m²/g, an aggregate size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between the particles, wherein said slurry is colloiddally stable.

18. The slurry of claim 1 wherein said particles are present in a range between about 0.5% and 55% by weight.

19. The slurry of claim 1 wherein said alumina particles have a surface area less than about 70 m²/g and are present in said slurry in a range less than about 7% by weight.

20. The slurry of claim 1 wherein said alumina particles have a surface area ranging between about 70 m²/g to about 170 m²/g and are present within said slurry in a range less than about 12% by weight.

21. The slurry of claims 19 or 20 wherein said alumina is a precipitated alumina or a fumed alumina.

22. The slurry of claim 1 wherein said particles have a maximum zeta potential greater than about ± 10 millivolts.

23. The slurry of claim 1 wherein said slurry further comprises a surfactant.

24. The slurry of claim 23 wherein the surfactant is selected from the group consisting of: nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants and mixtures thereof.

25. The slurry of claim 23 wherein said surfactant is selected from the group consisting of: polyalkyl siloxanes, polyaryl siloxanes, polyoxyalkylene ethers, and mixtures and copolymers thereof.

26. A chemical-mechanical polishing slurry for polishing a metal layer comprising high purity, alumina particles uniformly dispersed in an aqueous medium having a surface area ranging from about 40 m²/g to about 430 m²/g, an aggregate size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between the particles and an oxidizing component, wherein said slurry is colloiddally stable.

27. The slurry of claim 26 wherein said particles are present in a range between about 0.5% and 55% by weight.

28. The slurry of claim 26 wherein said alumina particles have a surface area less than about 70 m²/g and are present in said slurry in a range less than about 7% by weight.

29. The slurry of claim 26 wherein said alumina particles have a surface area ranging between about 70 m²/g to about 170 m²/g and are present within said slurry in a range less than about 12% by weight.

30. The slurry of claims 28 or 29 wherein said alumina is a precipitated alumina or a fumed alumina.

31. The slurry of claim 26 wherein said particles have a maximum zeta potential greater than about ± 10 millivolts.

32. The slurry of claim 26 wherein said oxidizing component is an oxidizing metal salt.

33. The slurry of claim 26 wherein said oxidizing component is an oxidizing metal complex.

34. The slurry of claim 26 wherein said oxidizing component is selected from the group consisting of: iron salts, aluminum salts, sodium salts, potassium salts, ammonium salts, quaternary ammonium salts, phosphonium salts, peroxides, chlorates, perchlorates, permanganates, persulfates and mixture thereof.

35. The slurry of claim 26 wherein said slurry further comprises an additive in an amount sufficient to prevent decomposition of the oxidizing component and maintain the colloiddal stability of the slurry.

36. The slurry of claim 35 wherein said additive is a surfactant.

37. The slurry of claim 35 wherein the surfactant is selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants and mixtures thereof.

38. The slurry of claim 36 wherein said surfactant is selected from the group consisting of: polyalkyl siloxanes, polyaryl siloxanes, polyoxyalkylene ethers, and mixtures and copolymers thereof.

39. The slurry of claim 26 wherein said alumina particle is fumed alumina comprising at least 50% gamma phase and said oxidizing component is iron nitrate.

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United States Patent [19]

Rostoker et al.

[11] Patent Number: **5,389,194**[45] Date of Patent: **Feb. 14, 1995**

[54] **METHODS OF CLEANING
SEMICONDUCTOR SUBSTRATES AFTER
POLISHING**

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Calif.**

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[73] Assignee: **LSI Logic Corporation, Milpitas,
Calif.**

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[21] Appl. No.: **77,809**

Primary Examiner—Brian E. Hearn

Assistant Examiner—Trung Dang

Attorney, Agent, or Firm—Honigman Miller Schwartz
and Cohn

[22] Filed: **Jun. 15, 1993**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 14,432, Feb. 5, 1993,
abandoned.

[51] Int. Cl.⁶ **H01L 21/306**

[52] U.S. Cl. **156/636; 437/228;
437/946; 252/79.3**

[58] Field of Search **252/79.3; 156/636;
437/228, 946; 51/281 R, 283 R**

[56] **References Cited**

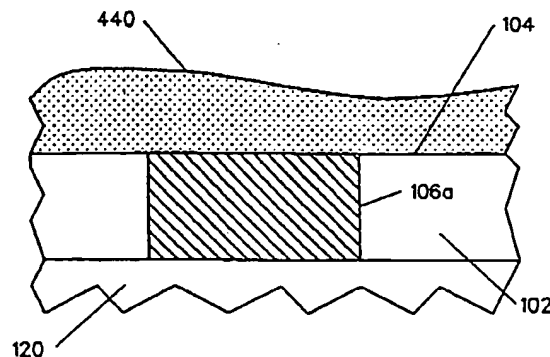
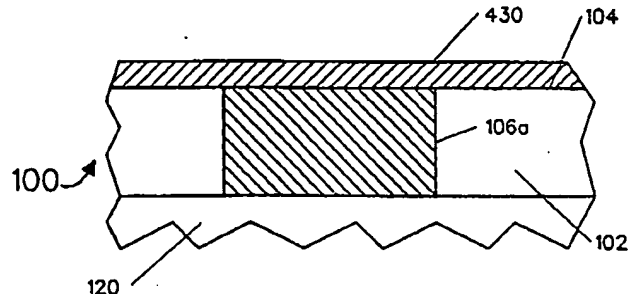
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[57] **ABSTRACT**

A method of cleaning semiconductor substrates after polishing, particularly chem-mech polishing a semiconductor substrate to planarize a layer, to remove excess material from atop a layer, and to strip back a defective layer is disclosed. Aluminum oxide particles having a small, well controlled size, and substantially in the alpha phase provide beneficial results when polishing. A phosphoric acid cleaning solution is used. The aluminum oxide particles are soluble in the phosphoric acid solution, which does not significantly attack silicon dioxide. The phosphoric acid solution can include a small concentration of hydrofluoric acid to aid in removing silicon dioxide detritus from the surface of the wafer.

25 Claims, 4 Drawing Sheets



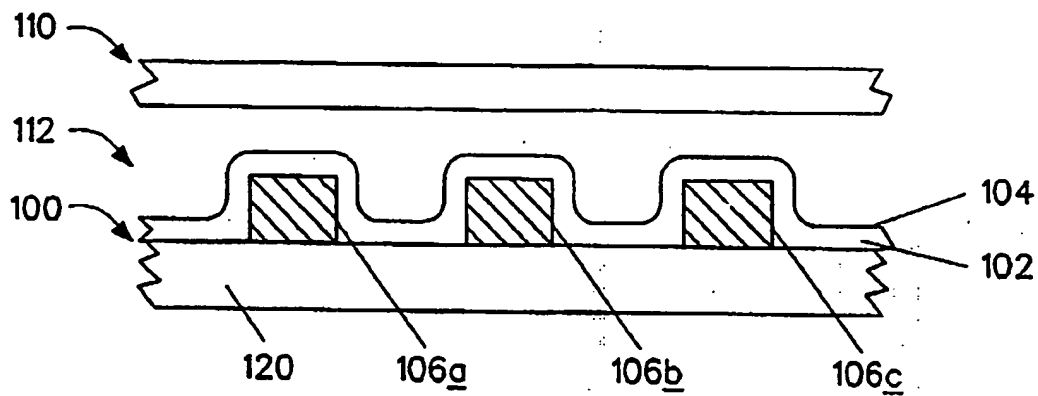


FIG. 1a

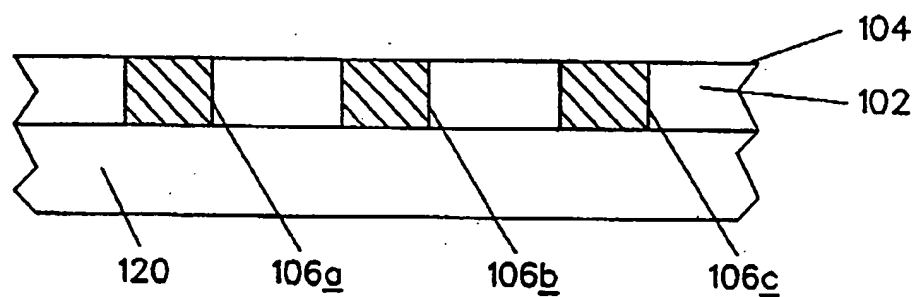


FIG. 1b

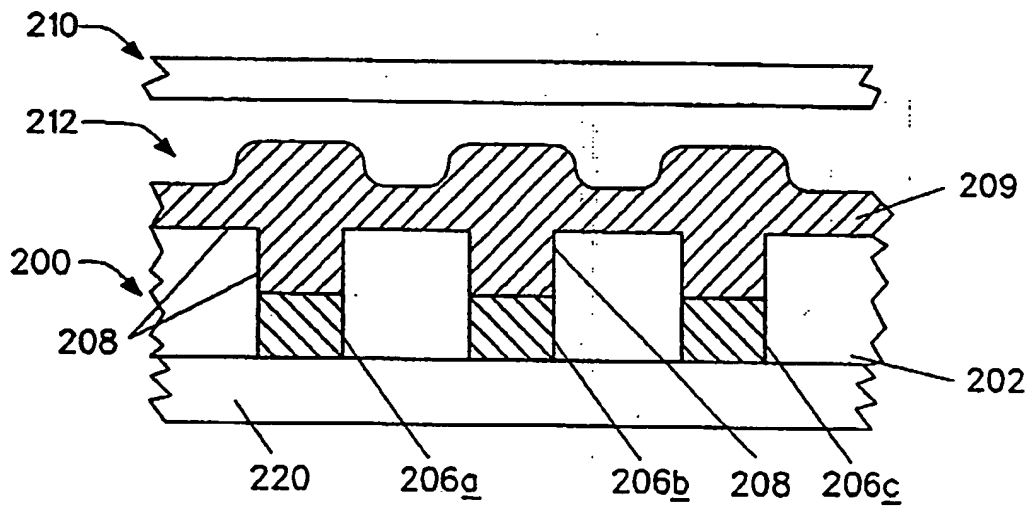


FIG. 2a

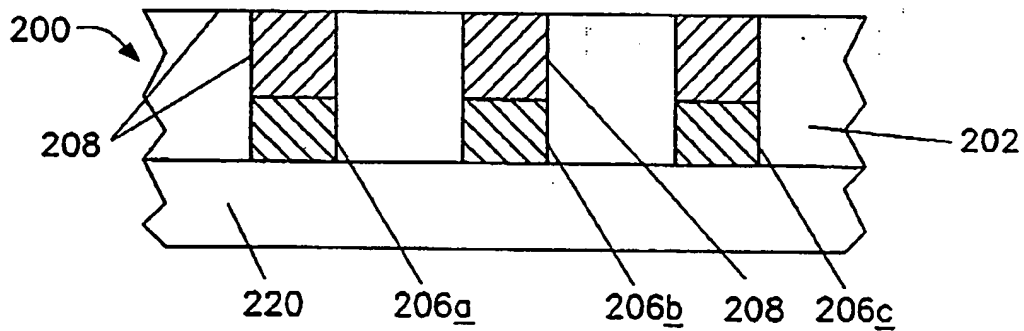


FIG. 2b

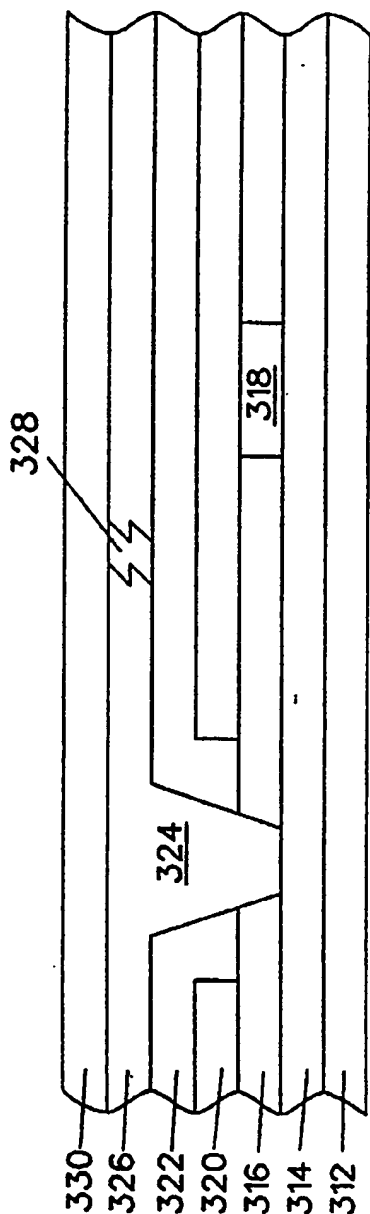


FIG. 3

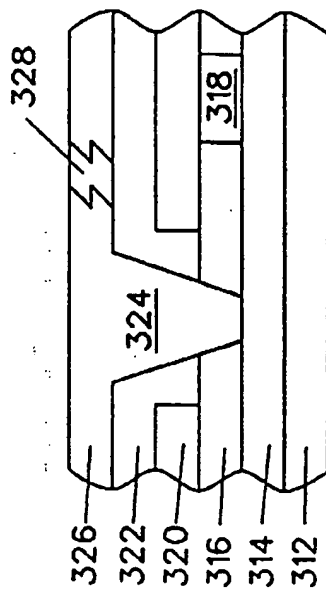


FIG. 3a

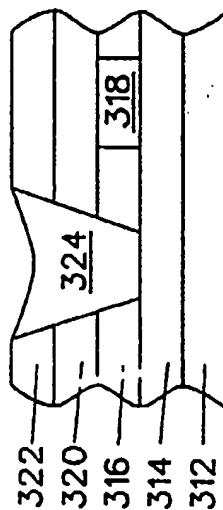


FIG. 3b

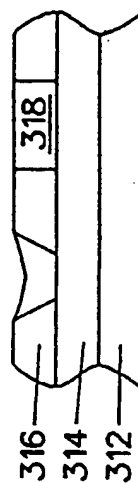


FIG. 3c

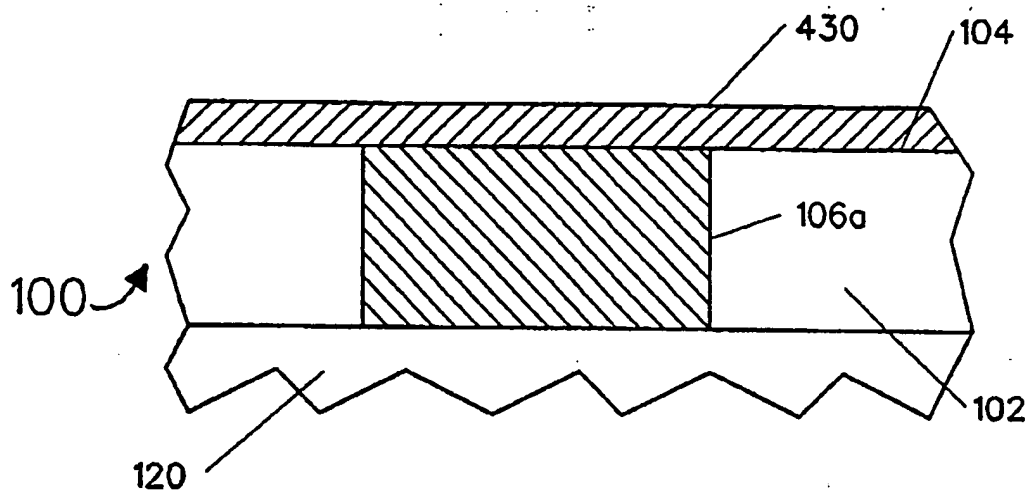


FIG. 4a

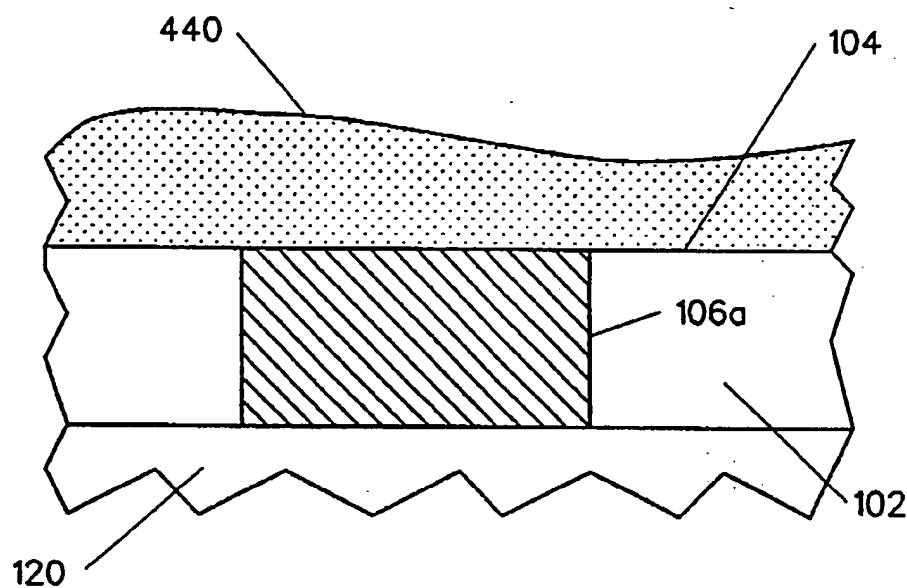


FIG. 4b

METHODS OF CLEANING SEMICONDUCTOR SUBSTRATES AFTER POLISHING

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. patent application Ser. No. 08/014,432, filed on Feb. 5, 1993, now abandoned by Rostoker.

TECHNICAL FIELD OF THE INVENTION

The present invention relates to processing steps in the fabrication or re-fabrication (e.g., repair) of semiconductor devices (e.g., wafers) and, more particularly, to the partial or complete polishing (stripping away) of layers previously deposited on the semiconductor device and, still more particularly, to the cleaning of the semiconductor device (e.g., wafer) after polishing.

BACKGROUND OF THE INVENTION

Semiconductor devices are fabricated step-by-step, beginning with a silicon wafer (substrate), implanting various ions, creating various circuit structures and elements, and depositing various insulating and conductive layers. Some of these layers are subsequently patterned by photoresist and etching, or similar processes, which results in topological features on the surface of the substrate. Subsequent layers over the topological layers inherit, and sometimes exacerbate, the uneven topology of the underlying layers. Such uneven (irregular, non-planar) surface topology can cause undesirable effects and/or difficulties in the application of subsequent layers and fabrication processes.

Hence, it is known, at various stages of semiconductor fabrication, to planarize a layer. Various techniques for planarizing a layer by etching or chemical-mechanical ("chem-mech") polishing are known. For example, chem-mech polishing of a semiconductor substrate is disclosed in U.S. Pat. Nos. 4,671,851, 4,910,155 and 4,944,836, incorporated by reference herein.

The present invention is directed to chem-mech polishing processes, which generally involve "rubbing" a wafer with a polishing pad in a slurry containing both an abrasive and chemicals. Typical slurry chemistry is KOH (Potassium Hydroxide), having a pH of about 11. A typical silica-based slurry is "SC1" available from Cabot Industries. Another slurry based on silica and cerium (oxide) is Rodel "WS-2000".

It is also known to use mechanical or chemical-mechanical (chem-mech) polishing techniques to completely remove (rather than to partially remove, or planarize) a layer that has been deposited. For example, U.S. Pat. No. 5,142,828, incorporated by reference herein, describes a process whereby a defective metallization layer is removed from the top of an electronic component such as an integrated circuit or a copper/polyimide substrate by polishing with a rotating pad and a slurry. Non-defective underlying metallization layers are preserved, and a new metallization layer is fabricated to replace the defective layer. For example, mechanical polishing of a copper layer, in a customizable high density copper/polyimide substrate, using a slurry of alumina grit with alumina particles between 0.05-3.0 microns suspended in solution, is disclosed in this patent. Slurries using silicon carbide and diamond paste are also described in the patent. The polishing of a tungsten layer is also suggested in the patent.

The aforementioned U.S. Pat. No. 4,910,155 discloses wafer flood polishing, and discusses polishing using 0.06 micron alumina particles in deionized water. The use of silica particulates is also discussed. Particulates of sizes as small as 0.006 microns (average size), and as large as 0.02 microns are discussed in this patent. The use of SiO₂ particulates (average diameter of 0.02 microns) suspended in water is also discussed in this patent.

Generally, chem-mech polishing is known for planarizing dielectric films. Generally, the penultimate layers of an integrated circuit are alternating dielectric and conductive layers forming interconnects, and the ultimate layer is a passivation layer, such as phosphosilicate glass (PSG). It is generally inconvenient and impractical to check the device at each step in the process since 1) functionally, the various gates and structures may not be interconnected at a particular stage, and 2) it is generally undesirable to remove the wafer from the "clean" fabrication environment at intermediate steps.

U.S. Pat. No. 4,956,313 discloses a via-filling and planarization technique. This patent discusses a planarization etch to remove portions of a metal layer lying outside of vias, while simultaneously planarizing a passivation layer, to provide a planarized surface upon which subsequent metal and insulator layers can be deposited. The use of an abrasive slurry consisting of Al₂O₃ particulates, de-ionized water, a base, and an oxidizing agent (e.g., hydrogen peroxide) is discussed, for etching tungsten and BPSG.

In the process of manufacturing semiconductor devices from silicon wafers, there is always the possibility that the device (or entire wafer) will be mis-manufactured. For example, a top metal layer (M_n) may exhibit voids reducing the cross-sectional area of conductive lines. Various other problems such as corrosion, mechanical stress and incomplete etching may be encountered. In the main hereinafter, voids in metal lines are discussed as an exemplary fault needing repair. Reference is made to "Stress Related Failures Causing Open Metallization, by Groothuis and Schroen, IEEE/IRPS, 1987, CH2388-7/87/0000-0001, pp.1-7, incorporated by reference herein.

Once a fault is identified, it can sometimes be repaired, and techniques such as focussed ion beam "micro-surgery" are known. However, in order to advantageously employ these repair techniques, or to remanufacture a defective layer it is necessary to strip off one or more of the top layers (e.g., passivation, metal, dielectric) of the device. These stripping techniques have as their goal returning the device (or a plurality of devices, when an entire wafer is processed in this manner) to a pre-existent, incomplete stage of manufacture, from which point onward, the device can be repaired or remanufactured.

Wet etching is one known technique for removing (stripping) layers of material in semiconductor devices. However, wet etching cannot be made to etch in any way except isotropically, which means that structures will be distorted in the horizontal (lateral) extent. Further, wet etching of oxide can destroy metal lines and bond pads.

Plasma etching, on the other hand, can be either isotropic or anisotropic, but it is usually unable to continue etching through all of the layers of material (e.g., oxide removal in the presence of metal lines) in the same cycle. This limitation forces the use of a series of different plasma etch processes, and simply does not work satisfactorily. In many instances, insulating layers un-

derlying metal areas are also etched away, with the result that the metal lines will lift off.

U.S. Pat. No. 4,980,019, entitled ETCH-BACK PROCESS FOR FAILURE ANALYSIS OF INTEGRATED CIRCUITS, (Baerg et al., Dec. 25, 1990) 5 discloses a method for etching exposed dielectric layer portions of an integrated circuit device to expose an underlying metal layer, by reactive ion etching (RIE) of the passivation layer. The technique is directed to etching back a delidded integrated circuit device.

U.S. Pat. No. 4,609,809, incorporated by reference herein, discloses method and apparatus for correcting delicate wiring of IC device employing an ion beam.

These techniques are unsatisfactory in that they alter the topography of the devices while film (layer) removal is taking place. In other words, they do not return the device to a truly pre-existent stage of fabrication. Consequently, significant losses in device throughput are incurred.

In any case, after chem-mech polishing, the surface of the wafer must be cleaned of debris, residue and detritus, and the like.

DISCLOSURE OF THE INVENTION

It is therefore an object of the present invention to provide an improved technique for polishing semiconductor devices.

It is a further object of the present invention to provide an improved technique for planarizing layers in semiconductor devices, including removing excess material such as metal overfilling vias.

It is a further object of the present invention to provide an improved technique for polishing back or removing layers in semiconductor devices.

It is a further object of the present invention to provide an improved technique for polishing back or removing layers in a semiconductor device as a prelude to reworking or repairing a defective layer in the device.

It is a further object of the invention to provide a technique for removing top layers of a semiconductor device, without damaging pre-existing topology, returning the wafer, undamaged, to a truly pre-existing state.

It is a further object of the present invention to provide an improved technique for chemical-mechanical ("chem-mech") polishing of semiconductor devices.

It is a further object of the present invention to provide an improved technique for chem-mech planarizing layers in semiconductor devices, including removing excess material such as metal overfilling vias.

It is a further object of the present invention to provide an improved technique for chem-mech polishing back or removing layers in semiconductor devices.

It is a further object of the present invention to provide an improved technique for chem-mech polishing back or removing layers in a semiconductor device as a prelude to reworking or repairing a defective layer in the device.

It is a further object of the invention to provide a 60 technique for removing top layers of a semiconductor device, by chem-mech polishing, without damaging pre-existing topology, returning the wafer, undamaged, to a truly pre-existing state.

It is a further object of the invention to provide a 65 technique for cleaning polishing residue from a semiconductor device which is compatible with the above-mentioned objects.

It is a further object of the invention to provide a technique for cleaning polishing residue from a semiconductor device which is compatible with the above-mentioned objects and which does not significantly 5 erode the polished surface of the semiconductor device.

It is a further object of the invention to provide a technique for cleaning polishing residue from a semiconductor wafer which effectively removes both detritus (debris from the polished layer) and residual polishing slurry, without significantly attacking the polished 10 (e.g., planarized) surface of the semiconductor device.

According to the invention, a semiconductor wafer is polished using particles of Aluminum Oxide (Al_2O_3) or Silica (SiO_2). Preferably, the particles are in a colloidal "suspension".

According to a feature of the invention, the Aluminum Oxide particles are preferably "Alpha" (α) state, but other forms of Aluminum Oxide (e.g., Gamma state, or pure Al_2O_3) may be used.

According to a feature of the invention, the Silica may be amorphous SiO_2 .

According to a feature of the invention, the size of the particles is on the order of 30-100 nm (nanometers), preferably approximately 50 nm.

According to a feature of the invention, the particles are used in a chemical-mechanical (chem-mech) "slurry", for chem-mech polishing a substrate.

According to a feature of the invention, the particles are used to remove unwanted structures, such as metal layers) from a finished or in-process substrate.

According to a feature of the invention, the particles are used to polish polyimide films or CVD TEOS layers.

According to a feature of the invention, the particles are used to planarize a layer or layers of an in-process semiconductor device. Such layer(s) may be dielectric films and/or metal layers, and such planarizing includes removing excess material such as metal overfilling vias.

According to a feature of the invention, the particles are used to remove a layer (or layers) of an in-process or substantially completed semiconductor device. Such layer(s) may be dielectric films and/or metal layers. The removed layer(s) may or may not be re-applied to the semiconductor device (substrate).

Preferably, an entire semiconductor wafer containing a plurality of semiconductor devices is polished with the particles, but individual dies (devices) can also be subjected to polishing with the particles.

According to a feature of the invention, the process of removing material from a semiconductor substrate with the particles is "surface-referenced", and the material removal process can be tailored to produce a resulting substrate surface which is either substantially planar or which is substantially conformal to underlying layers.

According to a feature of the invention, wafers which have been mis-manufactured can be returned to a pre-existing state, for repair (i.e., repair of the defective layer, followed by re-applying the overlying layers) or partial re-manufacture (i.e., re-applying the stripped off defective layer and overlying layers).

The use of the particles for polishing is a very effective way to prepare wafers for repair in the Back-End (BE) process. In this process, wafers are substantially completed, and their value to the manufacturer is maximized. Scrapping the wafers is costly and the loss of time to manufacture replacement wafers is at it's worst. In this case, a polish process can remove dielectric films back to the level of the BPSG reflowed glass layer. This

removal can take place at the Metal 1 layer, Interlevel dielectric (ILD), Metal 2 or Passivation Layers. In each case, if the metal is exposed to the polishing slurry, the metal will be removed back to the level of the silicon contacts. In this case, it is most optimal to polish back to the BPSG level.

The use of tungsten plug technology during metallization has certain beneficial effects in connection with the disclosed use of polishing for repair. Tungsten is not particularly attacked by basic polishing slurry. As such, the polish process does not automatically knock the metal level back to the contact level when upper metal levels are exposed to polishing slurry.

Aluminum, on the other hand, such as may be found in metal layers, may be severely attacked by the polishing slurry. Preferably, when polishing an aluminum layer, it is polished back to the contact level, since it is relatively difficult to remove aluminum in a via.

According to the invention, polishing residue, which includes detritus (debris) from the polished layer and residue from the polishing slurry, can be effectively cleaned from the semiconductor device using a phosphoric acid cleaning solution. An aluminum oxide particulate is considerably more soluble in the phosphoric acid cleaning solution than in the more conventional hydrofluoric acid cleaning solution used to remove residue from polishing silica-based slurries.

The phosphoric acid solution can contain a small concentration of hydrofluoric acid relative to the concentration of phosphoric acid. The hydrofluoric acid component in the cleaning solution serves to dissolve and remove any silicon dioxide polishing debris (detritus), which may result (e.g., from having polished a silicon dioxide layer or structure on the wafer. The relatively low concentration of hydrofluoric acid compared to that of phosphoric acid limits the amount of erosion of the polished layer. The relative concentration (e.g., molar) of hydrofluoric acid compared to that of phosphoric acid in the cleaning solution is, for example, less than 25%, 20%, 10%, 5%, 2%, 1%, or $\frac{1}{2}\%$.

Other objects, features and advantages of the invention will become apparent in light of the following description thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a is a cross-sectional view of a semiconductor device being polished, according to the present invention.

FIG. 1b is a cross-sectional view of the semiconductor device of FIG. 1a, after polishing.

FIG. 2a is a cross-sectional view of a semiconductor device being polished, according to the present invention.

FIG. 2b is a cross-sectional view of the semiconductor device of FIG. 2a, after polishing.

FIG. 3 is a cross-sectional view of a semiconductor device exhibiting a defect, according to the present invention.

FIG. 3a is a cross-sectional view of the semiconductor device of FIG. 3, after polishing.

FIG. 3b is a cross-sectional view of the semiconductor device of FIG. 3, after polishing.

FIG. 3c is a cross-sectional view of the semiconductor device of FIG. 3, after polishing.

FIG. 4a is an enlarged cross-sectional view of the semiconductor device of FIG. 1a, after polishing, showing a polishing residue.

FIG. 4b is a cross-sectional view of the semiconductor device of FIG. 4a, showing removal of the polishing residue.

It should be understood that while one semiconductor device may be shown and discussed, or only a particular portion thereof, the present invention is applicable to a plurality of such devices resident on a single silicon wafer.

DETAILED DESCRIPTION OF THE INVENTION

Technological progress is often based on the availability of new and improved materials which enable increasing the performance of new products or new methods of manufacture. For example, the discovery of the class of high temperature superconducting ceramics has given rise to numerous possible new products and new manufacturing methods. Frequently, progress in new material developments arises from the discovery of new chemical compounds or more sophisticated methods of manufacturing products, such as, new methods of miniaturization for use in integrated circuit manufacture.

Recently, methods have been developed for controllably producing ultrafine-grained, or nanocrystalline, materials (typically, about 1-100 nm grain diameters). These new methods have made possible the production of new materials having substantially different physical and chemical properties than the large grained, or single crystal, counterparts having substantially the same chemical composition.

U.S. Pat. No. 5,128,081, incorporated by reference herein, discloses a method of making nanocrystalline alpha alumina, and discusses providing substantially stoichiometric Al_2O_3 , and discusses providing nanocrystalline materials having selectable grain size. The patent discloses an apparatus for preparation of nanocrystalline or nanophase materials (hereinafter, "nanocrystalline" materials shall include crystalline, quasi-crystalline and amorphous phases). The patent discusses the preparation of nanocrystalline aluminum oxide, with a treatment that results in transformation of nanocrystalline aluminum powders (likely with a very thin oxide coating) to the thermodynamically stable alpha phase of aluminum oxide having an average particle size of about 18 nm. The patent discusses forming preferentially alpha alumina nanocrystalline ceramic material having a grain size of less than about 20 nm, and discusses alpha alumina having a median grain size of about 18 nm.

Given the recent advances in methods of producing such nanocrystalline materials, numerous problems in areas such as polishing semiconductor substrates can now be addressed using these new nanocrystalline materials.

According to the invention, aluminum oxide (Al_2O_3) particles are used to polish a semiconductor substrate. (Alumina is any of several forms of aluminum oxide, Al_2O_3 , occurring naturally as corundum, in a hydrated form in bauxite, and with various impurities such as ruby, sapphire, and emery, and is used in aluminum production and in abrasives, refractories, ceramics, and electrical insulation.)

The aluminum oxide particles are preferentially substantially entirely in the alpha phase. The alpha phase of aluminum oxide is harder than other phases of aluminum oxide, such as the gamma phase.

The aluminum oxide is preferably used in a chem-mech slurry for polishing the semiconductor substrate. Characteristics of the polishing particles:

According to the invention, the alpha aluminum oxide particles used for polishing exhibit the following characteristics. Preferably, the particle size is "X" nm, and the distribution of particle sizes is controlled to within "Y" nm, and the particles used for polishing are "Z" percent (%) in the alpha phase, where:

"X" is 10-100 nm, such as 10, 20, 30, 40 or 50 nm, and is preferably no greater than 50 nm; and

"Y" is approximately "P" percent of "X", where "P" is 10%, 20%, 30%, 40% or 50%, and is preferably no greater than 50% to ensure a narrow (Gaussian) distribution of particle sizes about "X";

"Z" is at least 50%, including at least 60%, 70%, 80% and 90%, and as high as 100%.

A quality factor "Q" is inversely related to "Y", and is a measure of the distribution of particle sizes. "Q" can be calculated as the concentration of particles at the desired size "X", divided by the range of sizes of particles at 3 db (decibels) lower than "X". Preferably, the size distribution of alpha aluminum oxide particles used for polishing exhibits a "Q" of at least 10, including 10, 50, 100, 500, 1000, 5000, or 10,000 ("Q" is dimensionless).

According to the invention, aluminum oxide particles exhibiting the aforementioned characteristics are used for planarizing a layer of a semiconductor device, such as an interlevel dielectric layer, a polyimide film, or a plasma etched CVD TEOS.

According to the invention, aluminum oxide particles exhibiting the aforementioned characteristics are used for stripping away a top metal layer, which may have been defectively applied to the semiconductor device.

According to the invention, aluminum oxide particles exhibiting the aforementioned characteristics are advantageous for use in polishing semiconductor devices because they can be supplied in a neutral state, then acidified or baseified at will, depending upon the layer to be polished. For maximum performance in polishing thermal oxide, a pH of 10.5 to 11 is desirable. For polishing metals, pH's as low as 3.0 to 3.5 are preferred.

Aluminum oxide exhibiting the aforementioned characteristics is superior to colloidal silica, since acidification of colloidal silica results in flocculation. Aluminum oxide remains in suspension under a wide range of pH's.

For polishing an aluminum layer, it is preferred to acidify aluminum oxide exhibiting the aforementioned characteristics with zinc sulphate. Increased acidification with alum is preferred. Glacial acetic acid is recommended for polishing other materials.

According to the invention, maintaining a high "Q" range of high percentage alpha phase aluminum oxide particles ensures superior polishing. For example, particles significantly larger than "X" tend to scratch the surface being polished, and particles significantly smaller than "X" are less effective in polishing and tend to dilute the slurry with relatively useless material.

In an alternate embodiment of the invention, gamma aluminum oxide is substituted for the alpha aluminum oxide described above.

In yet another embodiment of the invention, a colloidal suspension of amorphous silica is substituted for the alpha aluminum oxide described above.

Polishing to planarize:

FIG. 1a shows an in-process semiconductor device 100 having an layer 102 exhibiting a non-planar top surface 104. For example, the layer 102 is an interlevel dielectric layer (ILD) overlying a metal layer 106 having topological features such as conductive lines 106a, 106b and 106c. Prior to forming vias (not shown) through the ILD layer 102, it is desirable to planarize the top surface 104 of the layer 102. Hence, FIG. 1a shows a polishing pad 110 positioned to planarize the top surface 104 of the layer 102. A medium 112 containing particles (shown as dots ".") of alpha aluminum oxide is interposed between the polishing pad 110 and the top surface 104 of the layer 102. The layers 102 and 104 are formed atop a substrate 120.

FIG. 1b shows the semiconductor device 100 of FIG. 1a, after polishing. As shown, the top surface 104 of the layer 102 is substantially planar.

Polishing to remove excess material:

FIG. 2a shows an in-process semiconductor device 200 having a thick interlevel dielectric (ILD) layer 202 overlying a patterned metal layer 206 having conductive lines 206a, 206b and 206c. Vias 208 are formed through the ILD layer 202, in line with selected conductors 206a,b,c. A layer of metal 209 is applied over the ILD 202, to fill the vias 208, for interconnecting the lines 206a,b,c to a subsequent patterned layer of metal (not shown) overlying the ILD 202. At this point, it is desirable to remove the excess metal 209 overfilling the vias 208. Hence, FIG. 2a shows a polishing pad 210 positioned to remove the excess metal, while planarizing the top surface of the in-process substrate 220. A medium 212 containing particles (shown as dots ".") of alpha aluminum oxide is interposed between the polishing pad 210 and the top surface of the layer 209.

FIG. 2b shows the semiconductor device 200 of FIG. 2a, after polishing. As shown, the top surface of the layer 202 is substantially planar, the vias 208 are perfectly filled with metal 209, and there is no excess metal 209 outside of the vias 208.

Polishing to strip a layer:

FIG. 3 shows an idealized, substantially completed semiconductor device 300 displaying a defect. In this case open (or partially open) metallization will be discussed as a "generic" defect requiring re-working or repair of the device 300.

By way of example, in the fabrication process, the following steps proceed sequentially. First, lower layers 314 are deposited, patterned and the like on a substrate 312. The lower layers include any of a variety of depositions forming circuit structures, contacts and elements, as is known.

Next, by way of example, a layer 316 of Borophosphosilicate glass (BPSG) is deposited, which is a known technique for creating an intermediate planar topology for subsequent metal deposition.

Vias may be formed through the BPSG layer 316 to the lower layers 314, and filled by overlying metal. Alternatively, as shown, a tungsten plug 318 is formed atop the lower layers 314.

Next, a first, patterned metal layer ("M1") 320, formed of aluminum or an aluminum alloy, is deposited, creating a pattern of conductive lines.

Next, an intermetal insulating layer (ILD dielectric film) 322 is deposited. A via 324 is formed through the dielectric film 322 and through the BPSG layer 316 for connection of overlying metal to the lower layers 314.

Next, a second, patterned metal layer ("M2") 326, again formed of aluminum or an aluminum alloy, is

deposited, creating a pattern of conductive lines and filling the via 324.

As shown, the second metal layer 326 contains a void 328, which is a manufacturing defect generally undetectable at this stage of manufacturing.

Finally, a passivation layer 330, such as phosphosilicate glass (PSG) is deposited.

The resulting, substantially completed device can now be functionally tested. Such testing is expected to reveal the existence of the defect 328, and having been located and diagnosed, the task remains to strip off the passivation layer 330 and possibly the second metal layer 326 to repair or re-manufacture the second metal layer, respectively. To this end, the device 310 is subjected to chemi-mechanical polishing, as in FIGS. 1a and 2a.

FIG. 3a shows the device 300 after polishing, according to one embodiment of the invention. In this embodiment, the passivation layer 330 has been stripped (polished back) to the level of the second metal layer 326. At this point, it is possible to repair the defect 328 using a focussed ion beam, or other suitable repair technique.

FIG. 3b shows the device 300 after polishing, according to another embodiment of the invention. In this embodiment, the passivation layer 330 and the second metal layer 326 have both been stripped (polished back) to the level of the intermetal dielectric film 322. It would be expected that the metal in the via 324 would disappear if it is of the same material (aluminum) as that of the second metal layer 326. If the material in the via 324 is not severely attacked, it is possible to remanufacture (redeposit) the second metal layer (including any material removed from the via 324) and the passivation layer.

FIG. 3c shows the device 300 after polishing, according to yet another embodiment of the invention. In this embodiment, the passivation layer 330, the second metal layer 326, the intermetal dielectric film 322 and the first metal layer 320, in other words all of the upper layers, have been stripped (polished back) to the level of the BPSG layer 316. In this example, the tungsten plug 318 is exposed, but with most common polishing slurries (e.g., Cabot Industries Type SC-1) the tungsten will not be attacked.

Evidently, it is possible to polish back all the way to the contact level. In any case, the device 300 was substantially completely manufactured prior to polish back for repair. It is also possible that the polishing back technique could be applied at a somewhat earlier step, such as after deposition of first metal. By "substantially complete", it is meant that the fabrication of the device has proceeded to at least deposition of first metal.

Having thus described various applications for polishing semiconductor devices, there are set forth some exemplary polishing media.

EXAMPLE 1

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 50 nm; "Y" = 50%; and "Z" = 50%, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 2

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 50 nm;

"Z" = 50%; and "Q" = 100, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 3

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 10 nm; "Y" = 10%; and "Z" = 90%, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 4

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 10 nm; "Z" = 90%; and "Q" = 1000, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 5

As mentioned hereinabove, other phases of aluminum oxide, as well as silica, especially amorphous silica, can be substituted for the alpha phase, according to any of the previous examples.

Cleaning of the Semiconductor Device After Polishing

It is well known that after polishing a semiconductor device (e.g., 100, FIG. 1a; 200, FIG. 2a) to remove all or a portion of a layer (e.g., 104 FIG. 1a, 209, FIG. 2a), a film residue is left behind which must be cleaned. The film residue is composed primarily of the polishing slurry (e.g., 112, FIG. 1a; 212, FIG. 2a) and "detritus," or fine debris from the material of the layer which was polished. This is illustrated in FIG. 4.

FIG. 4a show a portion of the semiconductor device 100 (see FIG. 1b) after polishing. The ILD layer 102 has been polished back to a point where the conductive line 106a is exposed and flush with the surface 104 of the ILD layer 102. After polishing, however, a thin film of residue 430 remains. This residue comprises loose debris (detritus) from the polished layer 102 (and perhaps some detritus from the conductive line 106a) and left-over polishing medium and loose polishing particulate matter (e.g., aluminum oxide).

The effectiveness of subsequent processing of the semiconductor device 100 and the ultimate quality of the finished integrated circuit are dependent, in part, upon effective removal (cleaning) of the residue from the wafer. It is possible to remove at least part of the residue by simply "rinsing" the semiconductor device 100, because the residue comprises, in large part, loose particulate matter. However, such "rinsing" cannot guarantee complete cleansing of the wafer surface, and may leave "stubborn" particulate residue behind. Any extraneous matter (e.g., residue 430) remaining on the semiconductor device 100 after polishing has an adverse effect on subsequent processing steps. Evidently, more complete removal of the residue is required.

When polishing compounds based on silicon dioxide (silica) are used, it is known to remove the film residue (e.g., 430) by "washing" the semiconductor device with hydrofluoric acid. The silicon dioxide particles in the slurry is highly soluble in hydrofluoric acid, facilitating thorough removal of all of the slurry residue. If the layer being polished is also silicon dioxide, then the debris (detritus) from the polished layer will also be dissolved (and washed away). However, a certain amount of the exposed surface of the layer itself may

also be attacked by the hydrofluoric acid wash. It is evidently somewhat undesirable to remove material from the polished layer after the polishing process has terminated, since this would introduce an uncertainty into a process that is geared towards providing a polished surface of known characteristics.

When polishing compounds such as those described hereinabove (e.g. slurries based upon aluminum oxide particulate) or other polishing compounds based on polishing particles other than silicon dioxide are used, the effectiveness of cleaning with hydrofluoric acid is somewhat attenuated. These residual materials can be significantly less soluble in hydrofluoric acid than the material being polished, in which case the layer that was polished may be attacked more vigorously by the hydrofluoric acid than is the slurry residue. This can potentially lead to significant loss of layer thickness without effective removal of the polishing residue.

For polishing slurries based upon aluminum oxide and related materials, the polishing slurry and detritus can be effectively removed by using phosphoric acid or a solution of phosphoric acid and hydrofluoric acid. ("Related materials," in this context, means any polishing material which is relatively highly soluble in phosphoric acid). Aluminum oxide, for example, is effectively dissolved by the phosphoric acid, without significant dissolution of silicon dioxide. In other words, slurry residue containing aluminum oxide can effectively be removed without damaging an exposed layer of silicon dioxide (for example). The addition of small quantities of hydrofluoric acid to make a cleaning solution of phosphoric acid and hydrofluoric acid provides for removal of the silicon dioxide detritus, thereby cleaning the semiconductor device more effectively than by using only hydrofluoric acid or by using only phosphoric acid.

In FIG. 4b a cleaning solution 440 is disposed over the semiconductor device 100, substantially dissolving the film residue 430, while leaving the underlying ILD layer 102 relatively untouched. The cleaning solution 440 is primarily phosphoric acid. Assuming, however, that the ILD layer 102 is silicon dioxide, then a small amount of hydrofluoric acid is mixed with the phosphoric acid, to dissolve residual silicon dioxide detritus. As before, the hydrofluoric acid may attack the now polished and exposed surface of the ILD layer. However, by limiting the amount of hydrofluoric acid, this effect can be minimized.

The cleaning solution 440 can be either purely phosphoric acid (e.g., in some concentration, such as 10%, 20%, etc.), or can be a mixture of phosphoric acid and hydrofluoric acid containing a relatively low concentration of hydrofluoric acid. For example, there may be $\frac{1}{2}\%$, 1%, 2%, 5%, 10%, 20%, or 25% relative concentration of hydrofluoric acid vis-a-vis phosphoric acid in the cleaning solution for use in washing polishing residue from the surface of a semiconductor wafer. In any case, when polishing a layer of one material (e.g., silicon dioxide) with a slurry containing a different material (e.g., alumina), the cleaning solution contains at least a relatively high concentration of a solvent which is selective to the slurry residue, and a relatively small amount of a different solvent which is selective to the layer detritus.

What is claimed is:

1. A method of cleaning polishing residue from a semiconductor device, comprising:
providing a semiconductor device;

chemical-mechanically polishing a surface of the semiconductor device with an alumina-containing slurry, thereby leaving a polishing residue over the surface; and

cleaning the surface of the semiconductor device with a cleaning solution consisting essentially of a solution of phosphoric acid and hydrofluoric acid.

2. A method according to claim 1, wherein:

the cleaning solution has a relatively low concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid.

3. A method according to claim 2, wherein:

the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 25%.

4. A method according to claim 2, wherein:

the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 20%.

5. A method according to claim 2, wherein:

the concentration of hydrofluoric acid, as compared to the concentration of Phosphoric acid in the solution, is less than 10%.

6. A method according to claim 2, wherein:

the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 5%.

7. A method according to claim 2, wherein:

the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 2%.

8. A method according to claim 2, wherein:

the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 1%.

9. A method according to claim 2, wherein: the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than $\frac{1}{2}\%$.

10. Method of polishing a substrate, comprising:

polishing the surface of a semiconductor substrate with a medium of aluminum oxide particles having a preferred size "X" nanometers, a range of sizes within "Y" nanometers of "X" and a percentage "Z" of particles in the alpha phase, wherein:

"X" is 10-100 nm;

"Y" is "P" percent of "X", where "P" is no greater than 50%; and

"Z" is at least 50%; and

cleaning the surface of the semiconductor substrate with a cleaning solution consisting essentially of phosphoric acid and hydrofluoric acid.

11. A method according to claim 10, wherein:

the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 25%.

12. A method according to claim 11, wherein:

the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 20%.

13. A method according to claim 11, wherein:

the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 10%.

14. A method according to claim 11, wherein:

the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 5%.

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15. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of
hydrofluoric acid relative to that of phosphoric
acid of less than 2%.
16. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of
hydrofluoric acid relative to that of phosphoric
acid of less than 1%.
17. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of
hydrofluoric acid relative to that of phosphoric
acid of less than $\frac{1}{2}$ %.
18. Method of cleaning chemical-mechanical polish-
ing residue, including polishing slurry and substrate
debris, from a surface of a semiconductor wafer that
has been chemical-mechanically polished, comprising:
providing a cleaning solution of a first amount of
phosphoric acid and second amount of hydroflu-
oric acid, and no other acid, wherein the second
amount is less than 25% of the first amount; and

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cleaning the surface of the semiconductor wafer with
the cleaning solution.

19. Method, according to claim 18, wherein:
the polishing slurry contains alumina particles having
a size less than 50 nm; and

the alumina particles are primarily in the alpha phase.

20. Method, according to claim 18, wherein:
the second amount is less than 20% of the first
amount.

21. Method, according to claim 18, wherein:
the second amount is less than 10% of the first
amount.

22. Method, according to claim 18, wherein:
the second amount is less than 5% of the first amount.

23. Method, according to claim 18, wherein:
the second amount is less than 2% of the first amount.

24. Method, according to claim 18, wherein:
the second amount is less than 1% of the first amount.

25. Method, according to claim 18, wherein:
the second amount is less than $\frac{1}{2}$ % of the first amount.

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United States Patent [19][11] **Patent Number:** **5,300,130****Rostoker**[45] **Date of Patent:** **Apr. 5, 1994**[54] **POLISHING MATERIAL**[56] **References Cited**[75] **Inventor:** David Rostoker, Sturbridge, Mass.**U.S. PATENT DOCUMENTS**

4,657,754 4/1987 Bauer et al. 423/625

5,114,437 5/1992 Takeuchi et al. 51/309

5,149,338 9/1992 Fulton 51/309

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Ceramics Corp., Worcester, Mass.*Primary Examiner*—Mark L. Bell*Assistant Examiner*—Willie J. Thompson*Attorney, Agent, or Firm*—David Bennett[21] **Appl. No.:** 96,804[57] **ABSTRACT**[22] **Filed:** Jul. 26, 1993

A novel polishing slurry for particularly hard materials such a silicon carbide has been found. The slurry comprises diamond particles with a median particle size of around a micron and alpha alumina particles with a median size of from about 20 to about 200 nanometers.

[51] **Int. Cl.³** C09C 1/68[52] **U.S. Cl.** 51/309; 106/6[58] **Field of Search** 51/309; 106/6**10 Claims, No Drawings**

POLISHING MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to polishing materials particularly to polishing materials based on diamond that are used to produce fine finishes on hard materials.

Certain very hard ceramic materials are extremely difficult to polish to a fine finish unless a diamond polishing slurry is employed. Such materials include for example silicon carbide, aluminum/titanium carbide, tungsten carbide, aluminum nitride and alpha alumina monolith bodies. Diamond is very expensive and thus the polishing process itself is very costly.

Typical diamond slurries for this application contain diamond particles less than 2 microns in diameter and contain from about 10 to about 20 carats per liter of the diamond. The diamond particles need to be kept in suspension and this is typically done using suspending agents. U.S. Pat. No. 5,149,338 however teaches the use of a colloidal boehmite to maintain a diamond abrasive powder in suspension. This is said to yield a finish below 20 angstroms RMS when used on silicon carbide at a pH of 4. The boehmite has no significant abrasive qualities and is merely a means of presenting the diamond particles to the surface in a more efficient way. Moreover the pH used is severely corrosive of all but the best quality stainless steel, (or other resistant material), for the equipment contacted by the slurry. Other materials are available for polishing such hard ceramics including colloidal silica but while these are undoubtedly cheaper than diamond they are generally less effective and take much longer to achieve an acceptable finish.

There is therefore a need for a cheaper alternative to diamond for polishing hard materials that does not have a deleterious effect on the equipment used. This need is filled by the present invention which is more effective than diamond used alone and yet is quicker to achieve its desired surface finish. While not so cheap as colloidal silica it is substantially less expensive than a pure diamond polishing slurry.

DESCRIPTION OF THE INVENTION

The present invention provides an aqueous polishing slurry comprising diamond particles having a median particle size of less than 5 microns and alpha alumina particles with an average particle size of from 20 to 200 nanometers with a diamond to alumina weight ratio of from about 1:30 to about 1:90. Advantageously the slurry also comprises a suspending agent to maintain the dispersion of the diamond component.

The diamond component is a conventional polishing material as used in the prior art but need be used in much lower amounts than in conventional polishing slurries. These would typically comprise two to five grams of the diamond per liter of polishing slurry. The preferred slurries of the invention comprise less than 2 grams and conveniently from about 0.5 to about 1.5 gram of the same diamond per liter.

The alpha alumina component of the invention is a very finely divided material, and preferably one with a relatively narrow particle size distribution, for example one in which less than 5 volume percent of the particles have a size that is two or more times the volume average particle size of the alumina. Such materials can conveniently be obtained by the process described in U.S. Pat. No. 4,657,754. This process involves forming a sol of a hydrated alumina, adding a seed suitable for

the promotion of nucleation of the conversion of transition alumina to alpha alumina. Suitable seed include alpha alumina itself and other materials isostructural with alpha alumina and with lattice parameters closely related to those of alpha alumina, such as alpha ferric oxide, chromium oxide (in the Cr_2O_3 form) and various oxides and mixed oxides of titania. The sol of hydrated alumina can be gelled before or after the seed particles are added. The gelation can be done by acid peptization or by reducing the water content. Thereafter the gel is dried and then fired to a temperature and for a period to convert most of the alumina to alpha alumina but insufficient to cause significant sintering of the alpha alumina particles to occur. This resulting product is relatively easily milled to a powder of the desired particle size and size distribution. Thus the preferred alumina powder is a seeded sol-gel alpha alumina.

DETAILED DESCRIPTION OF THE INVENTION

The preferred polishing compositions of the invention are in the form of slurries comprising from about 0.8 to about 1.5 grams per liter of diamond particles with a median particle size of from about 0.5 to about 2.5, and more preferably from about 0.8 to about 1.5 micron. These preferred slurries also comprise from about 40 to about 80 grams per liter of an alpha alumina having a median particle size of from about 20 to about 200, and more preferably from about 40 to 100 nanometers. These alpha alumina particles are preferably produced by a seeded sol-gel process and may contain a minor amount, such as up to about 25% but preferably less than about 10%, by weight, of a transitional alumina such as gamma alumina.

The polishing slurry also preferably contains a suspending agent in an amount that is effective to maintain the diamond particles in suspension. There are many known commonly available suspending agents which are capable of performing this function such as xanthan gum, magnesium aluminosilicate clays, certain acrylic polymers and carboxymethyl cellulose. The effective amount will of course vary with the agent used. Generally an effective amount for xanthan gum is about 1 to 5 grams per liter for the amounts of diamond that are preferably involved.

In addition the slurry can contain other additives with specific functions not related to the abrasive performance such as bactericides and in some cases buffers. Unlike some of the prior art slurries, the pH of the compositions of the present invention is preferably maintained above 7 and often about 10. This avoids the corrosive problems of working at acid pH values that characterize some of the prior art slurries.

One significant advantage of the slurries of the invention is that they can be recycled until the swarf build-up renders them ineffective. In normal use, this can take as long as two to three weeks.

The slurries of the invention can be used with any conventional type of lapping pad or pitch lap. However the best results are often obtained using a pad that is relatively hard such as a polyurethane pad filled with glass beads and sold by Rodex Corporation under the trade designation IC-60. The slurries of the invention can be used to polish in either a single side or a double sided mode.

The applied weight on the pad during polishing can be in the range that is conventionally used for such

applications. However pressures at the higher end of the normal range can be used without detriment and this results in a faster cycle time without significant loss of surface quality.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention is now described with reference to the following examples which are for the purpose of illustration only and are not intended to imply any necessary limitation of the essential scope of the invention.

TABLE 1

Descrip.	Exp. #1	Exp. #2	Exp. #3	Exp. #4	Exp. #5	Exp. #6	Exp. #7	Exp. #8
Lapping Material	Pit.	Pit.	Pit.	IC 60	IC 60	IC 60	IC 60	IC 60
Pol. Ag.	B + D	B + D	B + D	A + D	A + D	A + D	A + D	A
Al. Size	200 Ang.	50 nM	50 nM	50 nM	50 nM	1.0 Micr.	50 nM	50 nM
Al. Vol.	4 oz	4 oz	4 oz	250 ml/l	250 ml/l	250 ml/l	250 ml/l	250 ml/l
Al. %	17%	17%	17%	22%	22%	22%	22%	22%
Solids								
D. Size	2-4	2-4	2-4	1	1	1	1	
Microons								
D. Conc	2.5	2.5	2.5	1.0	16	5	4	
(ct/l)								
Weight	5	5	5	46.5	46.5	46.5	46.5	46.5
(lbs)								
Time	2	—	4	1.5	.75	1.5	.75-1.0	1.5
hours								
Finish	10/90	—	0/35	5/80	5/40	40/550	5/35	150/1000
RMS/TIR								
Water	4 oz.	4 oz.	4 oz.	750 ml + Gum	750 ml + Gum	750 ml + Gum	750 ml + Gum	750 ml + Gum
Amnt.								

EXAMPLE 1

The purpose of this Example is to demonstrate the improvement represented by the slurries of the present invention over the art as represented by the sole Example contained in U.S. Pat. No. 5,147,338 (discussed above).

Run #1 is a replication, in different equipment, of the Example in the above patent using all other conditions as specified therein. Run #2 was the same as Run #1 except that the alumina particle size was changed from 200 angstroms to 50 nanometers. Run #3 repeated Run #2 except that xanthan gum was added to keep the diamond in suspension. It will be noted from the results that in Run #2 the absence of the suspending boehmite that was present in Run #1 had disastrous results.

Runs #4, #5 #6 and #7 are according to the invention and show the effect of varying the amount of diamond and the particle size of the alumina. Comparison of Runs #5 and #7 show that there is little or no benefit from quadrupling the amount of diamond, and Run #6 shows that increasing the alumina particle size to an average particle size of one micron has a very negative effect on the performance. Run #8 duplicates Run #7 but without the diamond component. As can be seen the excellent properties of the compositions of the invention are not obtained using the alumina component alone.

In Table 1 below the following abbreviations are used: "A" is alpha alumina, "B" is boehmite and "D" is diamond. "Pit." is a commercial pitch available from Gugolz GmbH of Winterthur, Switzerland under the designation "CH84-04". This is similar to pitch used in U.S. Pat. No. 5,149,338 as the polishing tool. "Weight" is the applied load on the polishing tool. "Time" is the time taken to achieve the indicated finish. "RMS" is the calculated average amplitude of the peaks and valleys

over an 80 micron traverse of a diamond stylus across the surface.

The units are angstroms. "TIR" is the greatest peak-to-valley distance, in angstroms, measured during the traverse that yielded the RMS result. Both RMS and TIR were measured using a "Tencor Alpha-Step 200" available from the Tencor Corporation.

The "Gum" added during the Experiments that exemplified the invention was xanthan gum and was used to keep the diamond in suspension.

Except for #1, where the pH was 4, the pH was maintained at 10.05

From the data in the above Table it is clear that the process of the prior art patent is not capable of yielding improved results merely by making the boehmite particles larger, indeed the results were so bad in Exp. #2 that no values could be obtained for the finish. Nor was the addition of gum the answer for although a good finish was obtained, it took four hours to obtain it.

The data in the Table also show that excellent results are obtained in a very short time using alpha alumina but that the results deteriorate drastically, (Expt #6), if the alpha particle size becomes comparable to that of the diamond component.

EXAMPLE 2

This Example shows the utility of the compositions of the Invention in the polishing of a number of very hard materials in comparison with diamond used alone.

In each case the diamond component had the same size, (about one micron) and was used in the same quantity, (5 ct/l). The alpha alumina used had a median particle size of 50 nanometers and was used in a concentration of 66 gram/liter. In each case the same amount of xanthan gum was used to maintain the dispersion of the components.

The results appear in Table 2 below.

TABLE 2

Material	Polish	Time Hr.	RMS	TIR
SiC (Hot Press)	D/A	1.0	5	35
SiC (Hot Press)	D	1.0	15	70
Al TiC	D/A	1.0	7	60
Al TiC	D	1.5	10	70
WC	D/A	.5-.75	5	50
AlN	D/A	1.5	140	700
IBM Alumina	D/A	2	165	1000

TABLE 2-continued

Material	Polish	Time Hr.	RMS	TIR
CPS Alumina	D/A	1	225	1600

The abbreviations "D", "A", "RMS" and "TIR" are as explained for Table 1 and the RMS and TIR units are angstroms. The aluminum nitride, (AlN), contains a higher proportion of binder that leads to significant grain "pull-out" during polishing. This is also true of the IBM and CPS aluminas polished. Both are fully fired aluminas with about 10 to 15% of a binder.

These results clearly demonstrate that the diamond/alumina compositions of the invention possess a striking synergistic effectiveness that is not matched by either component alone.

What is claimed is:

1. A polishing slurry comprising diamond particles having a particle size less than 5 microns, alpha alumina particles with an average particle size of from 20 to 200 nanometers and an amount of a suspending agent effective to maintain the diamond particles in suspension; the slurry having a diamond to alumina weight ratio of from about 1:30 to about 1:90.

2. A polishing slurry according to claim 1 in which the diamond particle have a median particle size of from about 0.5 to about 1.5 micron.

3. A polishing slurry according to claim 1 in which the alpha alumina particles have a median particle size of from about 40 to 5 about 100 nanometers.

4. A polishing slurry according to claim 1 in which the diamond to alumina weight ratio is from about 1:50 to about 1:80.

5. A polishing slurry according to claim 1 in which the solids content is from about 40 to about 80 grams per liter.

6. A polishing slurry according to claim 1 in which the suspending agent is xanthan gum.

7. A polishing slurry according to claim 6 in which the amount of the xanthan gum is from about 1 to about 5 gm/l.

8. A polishing slurry comprising from about 1 to 10 carat/liter of diamond particles having a median particle size of from about 0.2 to about 1.0 micron, from about 30 to about 90 grams/liter of alpha alumina particles with an median particle size of from about 40 to about 100 nanometers and an amount of a suspending agent effective to maintain the diamond particles in suspension; the slurry having a diamond to alumina weight ratio of from about 1:40 to about 1:80.

9. A polishing slurry according to claim 8 in which the suspending agent is xanthan gum.

10. A polishing slurry according to claim 9 which comprises from about 1 to about 5 gm/liter of xanthan gum as the suspending agent.

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United States Patent [19]
Zipperian

US005228886A

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[45] Date of Patent: Jul. 20, 1993

[54] MECHANOCHEMICAL POLISHING
ABRASIVE

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[21] Appl. No.: 753,654

[22] Filed: Aug. 30, 1991

Related U.S. Application Data

[63] Continuation of Ser. No. 594,065, Oct. 9, 1990, abandoned.

[51] Int. Cl.³ B24D 3/00

[52] U.S. Cl. 51/293; 51/308;
51/309

[58] Field of Search 51/293, 308, 309

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[57] ABSTRACT

A mechanochemical polishing abrasive and a process for using the mechanochemical polishing abrasive to polish the surface of a hardened workpiece cheaply and efficiently. The mechanochemical polishing abrasive comprises a slurry of colloidal silica and a mechanical abrasive selected from one or more of the materials in the group comprising Fe_2O_3 , Fe_3O_4 , MgO , $BaCO_3$, $CaCO_3$, MnO_2 , CeO , SiO_2 , CeO_2 , Cr_2O_3 , and Al_2O_3 .

16 Claims, No Drawings

MECHANOCHEMICAL POLISHING ABRASIVE

This is a continuation of application Ser. No. 07/594,065, filed Oct. 9, 1990, aban. Apr. 16, 1992.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is a mechanochemical polishing abrasive for use in the polishing of hard substrates such as ceramics, crystalline materials, glass and similar materials which require highly polished surfaces.

The economics of polishing and machining ceramics can often be the most costly part of the ceramic production process. Economic considerations for polishing ceramics involve both the time and the consumable products employed. For final polishing of ceramics, diamond abrasives are extensively used, the diamond abrasives are expensive and the polishing process using diamond abrasives is slow.

Conversely, the machining of ceramics can be very damaging. Unlike the machining of metals which are ductile, ceramics are generally very brittle. The brittle nature of ceramics makes them very sensitive to subsurface fracturing. This subsurface damage adversely affects significant physical properties of the ceramics. Such physical properties adversely affected by machining include a reduction in the ceramics strength, changes in the ceramic magnetic properties, and even changes in the electronic properties of the ceramics.

The machining of advanced ceramics has traditionally been accomplished by hard abrasives such as diamond or silicon carbide. Though this has produced surfaces that are acceptable under certain circumstances, there still remains a certain degree of surface and subsurface damage utilizing these compounds. The use of softer polishing abrasives, such as colloidal silica, for machining advanced ceramics has been examined. Colloidal silica has been shown to polish alumina, silica, and silicon.

In fact, colloidal silica has been used extensively to polish silicon chips. However, the use of colloidal silica to polish advanced ceramics tends to produce a polished advanced ceramic product with substantial phase relief. The relief is believed to be caused by the chemical dissolution of selective grains on the advanced ceramics by the colloidal silica.

2. To Prior Art

The use of colloidal silica to polished silicon surfaces, metals, glass, garnets and sapphires is disclosed in the article H. W. Gutsche and J. W. Moody, "Polishing of Sapphire with Colloidal Silica", *J. Electrical Chemical Soc.* 125, No. 1, Pages 136-138, (1978). The article discloses that colloidal silica has a chemical effect on the harder sapphire material allowing the colloidal silica to polish the sapphire. The article is silent concerning combining colloidal silica with other polishing substances to polish hardened materials.

The use of CaCO_3 , BaCO_3 and MgO as mechanochemical polishing abrasives is disclosed in a report by H. Bora and R. J. Stokes, *Study of Mechanochemical Machining of Ceramics and the Effect on Thin Film Behavior*, United States Government Report N00014-80-C-0437-1 (Apr. 30, 1981). The report details the polishing of thin layers of MgO , Al_2O_3 and Si by various abrasives including rock salt, Calcite, Fluorite and various other abrasives including window glass. The three compounds mentioned above were discovered to be

capable of mechanochemically polishing one or more of the above materials. None of the mechanochemical abrasives used were combined with colloidal silica.

The mechanochemical polishing of sapphire, silicon, and quartz crystals is disclosed by N. Yasunaga, U. Tarumi, A. Obara, "Mechanism and Application of the Mechanochemical Polishing Method Using Soft Powder" *The Science of Ceramic Machining and Surface Finishing II*, NBS special publication 562, U.S. Government Printing Office, Washington, D.C., pages 171-183 (1979). The sapphire, silicon and quartz were polished with wet and dry mechanochemical media. The mechanochemical media included BaCO_3 , Fe_3O_4 , CeCO_2 , SiO_2 , CeO_2 , diamond and MnO_2 . The primary focus of the article is a description of the formation of crystalline silica materials in the mixed powder abrasive during the workpiece polishing. The crystalline materials were produced by polishing the hard materials described above at high temperatures and pressures using the mixed powder. The article does not disclose the use of colloidal silica in any manner for mechanochemical polishing.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an inexpensive mechanochemical polishing abrasive which is capable of polishing a hardened work piece without selectively abrading the surface particles of the hardened work piece.

It is yet another object of this invention to provide a method for polishing a hardened work piece utilizing an inexpensive mechanochemical abrasive. This invention relates generally to a mechanochemical abrasive. The mechanochemical abrasive comprises a slurry of colloidal silica containing one or more mechanical abrasives.

In a variation of this embodiment, this invention is a mechanochemical abrasive comprising a slurry of colloidal silica and a mechanical abrasive selected from one or more of the materials in the group comprising Fe_2O_3 , Fe_3O_4 , MgO , BaCO_3 , CaCO_3 , MnO_2 , CeO , SiO_2 , CeO_2 , Cr_2O_3 , and Al_2O_3 .

In a preferred embodiment, this invention is a mechanochemical polishing abrasive comprising from about 13 to about 99.3 weight per cent of a basic slurry of colloidal silica and from about 0.7 to about 2.0 weight percent of a mechanical abrasive. The mechanical abrasive has a particle size of from about 0.1 microns to about 10 microns. The mechanical abrasive is selected from one or more of the materials in a group comprising Fe_2O_3 , Fe_3O_4 , MgO , BaCO_3 , CaCO_3 , MnO_2 , CeO , SiO_2 , CeO_2 , Cr_2O_3 , and Al_2O_3 .

In another embodiment, this invention is a method for polishing one or more workpieces with a mechanochemical polishing abrasive. The mechanochemical polishing abrasive comprises an aqueous slurry of colloidal silica and a mechanical abrasive selected from one or more of the materials in the group comprising Fe_2O_3 , Fe_3O_4 , MgO , BaCO_3 , CaCO_3 , MnO_2 , CeO , SiO_2 , CeO_2 , Cr_2O_3 , and Al_2O_3 . The workpiece is polished by applying the mechanochemical polishing abrasive to a workpiece and either directly or via a polishing pad and contacting the polishing means with one or more workpieces for a period of time sufficient to polish a surface of the workpiece.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to mechanochemical polishing abrasive and a method for polishing a workpiece utilizing the mechanochemical polishing abrasive. The mechanochemical polishing abrasive of this invention comprises a colloidal silica material combined with a mechanical abrasive.

The colloidal silica material contained in the mechanochemical polishing abrasive of this invention chemically reacts with the various surface components which make up the hardened workpieces that are polished with the mechanochemical polishing abrasive. The precise chemical reaction that occurs between the colloidal silica and the elements and molecules in the surface of the workpiece is not totally understood. However, it is believed that the colloidal silica reacts with the surface of the hardened workpiece to produce a surface material on the workpiece that is softer than the mechanical abrasive. As mentioned above, one drawback with the colloidal silica is that it appears to attack preferred grains on the surface of the hardened substrate so that a relieved surface finish can result when the workpiece surface is chemically altered by the colloidal silica.

Colloidal silica is typically supplied in an aqueous (water-containing) slurry made up of up to 50% or more colloidal silica. One interesting feature of the colloidal silica slurry is that the colloidal silica does not settle from a slurry even after a great period of time. The colloidal silica is generally contained in an aqueous slurry, that is combined with water. However, for purposes of the polishing abrasive of this invention, the colloidal silica need not be, and in some cases, must not be in a slurry with water, but can be in a slurry with some other liquid, such as an alcohol and organic solvent or the like material. Water is not desired as a slurry of material in all cases because water can adversely react with certain hardened workpieces to produce a useless product.

The preferred colloidal silica will be an aqueous slurry of colloidal silica. The weight percent content of the colloidal silica in the aqueous slurry is not critical. However, it is preferred that the colloidal silica be present in the aqueous slurry in an amount ranging from about 15 to about 50 weight percent or greater.

Other properties of the colloidal silica slurry such as pH, particle size and the like are not absolutely critical to its usefulness in chemically reacting with the surface of a hardened workpiece. However, it is preferred that the pH of the colloidal silica slurry be greater than about seven. A colloidal silica slurry having a pH greater than about seven is a basic slurry, and has been found to react more efficiently with the surface of the materials which can be polished with the mechanochemical polishing abrasive of this invention.

The preferred aqueous slurry of colloidal silica can be any known colloidal silica slurry. Generally, colloidal silica's are stabilized at a pH of from about 8 to 14 and more commonly in a range from about 9 to 11. The preferred colloidal silica has a pH ranging from about 9.8 to 10.2 and has an average particle size of about 0.06 microns.

The mechanochemical polishing abrasive of this invention also includes a mechanical abrasive. The mechanical abrasive is generally a softer material than the material making up the workpiece. However, the mechanical abrasive is generally harder than the surface

material of the workpiece resulting from the chemical reaction between the colloidal silica components of the polishing abrasive and the hardened workpiece. The purpose of the mechanical abrasive is to abrade the softer reacted materials from the surface of the hardened workpiece leaving behind a smooth workpiece surface. By abrading the softer reaction product from the surface of the hardened workpiece the mechanical abrasive continuously exposes a hardened surface to the colloidal silica which chemically reacts with the exposed surface. In this way, the selective reaction of the colloidal silica with various selective grains on the surface of the hardened workpieces can be reduced to a minimum producing a highly polished, hardened substrate surface.

The mechanical abrasive useful in the mechanochemical abrasive of this invention may be any material or combination of materials known in the art to be useful as a mechanical abrasive material. The mechanical abrasive will typically be softer, that is, not as hard as the material making up the workpiece. The mechanical abrasive material may, for example, be selected from one or more of the following compounds: Fe_2O_3 , Fe_3O_4 , MgO , BaCO_3 , CaCO_3 , MnO_2 , CeO , SiO_2 , CeO_2 , Cr_2O_3 , and Al_2O_3 . A preferred mechanical abrasive is Fe_2O_3 . It is also preferred that the mechanical abrasive have an average particle size of from about 0.1 microns to about 10 microns and more preferably from about 0.5 to 5.0 microns.

As previously mentioned, the mechanochemical polishing abrasive of this invention comprises a slurry of colloidal silica and one or more mechanical abrasives. The mechanochemical polishing abrasive of this invention will typically contain from about 0.1 grams of a powdered mechanical abrasive with 100 ml of colloidal silica to enough mechanical abrasive combined with colloidal silica to turn the mechanochemical polishing abrasive into a viscous slurry. The amount of mechanical abrasive necessary to turn the mechanochemical abrasive into a viscous slurry will vary depending upon the mechanical abrasive used and depending upon the silica content of the colloidal silica.

Water or other diluent materials such as alcohols, solvents, etc. may be added to the mechanical abrasive/colloidal silica mixture to reduce the viscosity of the mechanochemical abrasive. A mechanochemical abrasive with a low viscosity is easily applied to workpieces. It covers the workpieces evenly and generally has better flow and abrasive properties.

Preferably, the mechanochemical abrasive of this invention will comprise from about 0.07 to about 2.0 wt % of a powdered mechanical abrasive from about 13 to about 99.2 wt % of colloidal silica and from about 0.7 to about 85 wt % ml water. Preferably, the water is deionized water.

The mechanochemical abrasive of this invention is useful for polishing the surfaces of many different hardened workpieces. The mechanochemical polishing abrasive of this invention may be used to polish the surface of any material which is capable of chemically reacting with a colloidal silica slurry. Examples of such material include silicon (such as silicon wafers), sapphire, metals, glass, alumina, silicon nitride (Si_3N_4), gallium arsenide (GaAs), magnesium oxide (MgO), zirconia and other hardened ceramic and non-ceramic materials.

The mechanochemical polishing abrasive of this invention can be used to polish hardened workpieces by

any polishing means known in the art for polishing hardened workpieces. The polishing can be accomplished by any polishing means including by hand using a pad and the mechanochemical polishing abrasive, or by a machine using the liquid mechanochemical polishing abrasive of this invention. It is preferred that a pad be used in conjunction with a machine to polish hardened workpieces with the polishing abrasive of this invention. The polishing abrasive is applied to the pad or the workpieces and the pad then frictionally contacts at least one surface of the abrasive covered workpieces during the polishing step. The workpiece is polished for a period of time sufficient to polish the surface of the workpiece to a desired finish.

Polishing conditions, including pressure and temperature, may affect workpiece polishing rate. However, the abrasive is effective in polishing workpieces over a wide range of pressures and temperatures. Specific pressures and temperatures are not required for the mechanochemical polishing abrasive to be effective.

Certain preferred examples of the invention will be discussed below. However, many other examples would also fall within the scope of present invention.

EXAMPLES

EXAMPLE 1

In this example Alumina (Al_2O_3) was polished with various abrasives including mechanical abrasives, chemical abrasives and the mechanochemical abrasive of this invention. The abrasives were evaluated for their ability to remove surface material from alumina workpieces over time.

The surface of the alumina workpieces were prepared by grinding them with 30 micron diamond particles contained on a hard polymer composite plate followed by grinding with 6 micron diamond particles on a soft polymer composite plate. After the surface of the alumina was prepared, a Knoop indent was made in the hardened workpiece with a 5 kg load, indented at a loading rate of 70 microns/sec. with a loading time of 15 seconds. Material removal rates were made by measuring the reduction in the diagonal length of the Knoop indent over time.

Both vibratory and semi-automated polishers were used. Vibratory polishing was used to minimize the mechanical contribution. The experiments were monitored for 24 hours. Semi-automated polishers were used to provide added mechanical contribution.

The polishing was conducted on a TEXMET® polishing cloth sold by Buehler.

A summary of the polishing results for alumina workpieces is found in Table I below:

TABLE I

Polishing Technique	Abrasive	Polishing Rate (microns/hr)
Vibratory Polishing	Fe_2O_3	0.002
	colloidal silica	0.042
	Fe_2O_3 + (colloidal silica)	0.125
Mechanical Rotary Polishing	Fe_2O_3	nil
	colloidal silica	0.26
	1/2 microns diamond	nil
	3 microns diamond	0.21
	Fe_2O_3 + (colloidal silica)	0.35

The results indicate that, with either vibratory or mechanical rotary polishing, the mechanochemical pol-

ishing abrasive of this invention comprising colloidal silica slurry in combination with the mechanical abrasive, Fe_2O_3 , is able to polish alumina at a higher polishing rate than either colloidal silica or Fe_2O_3 alone. Additionally, the polishing rate for the colloidal silica/ Fe_2O_3 abrasive is far superior to the cumulative polishing rate of the colloidal silica and the Fe_2O_3 . (0.125 microns/hr versus 0.044 microns/hr for vibratory polishing and 0.35 microns/min. versus 0.26 microns per min. for rotary polishing).

This example clearly shows that the mechanochemical polishing abrasive of this invention unexpectedly has a superior polishing rate in comparison to colloidal silica or mechanical abrasives alone or cumulatively.

EXAMPLE II

Using the same vibratory polishing method above, Knoop indented samples of alumina, silicon nitride, and zirconia were polished using colloidal silica, various mechanical abrasives and various mechanochemical abrasives of this invention.

The mechanochemical polishing media consisted of a liter of solution made up of 20 grams of either Al_2O_3 , Ce_2O_3 , Cr_2O_3 or Fe_2O_3 along with, 490 ml of a aqueous colloidal silica. The aqueous colloidal silica had a pH of about 10.0, an average particle size of about 0.05-0.07 microns, a specific gravity of 1.390 and contained 50% solids. 5 ml of deionized water was added to the mixture to complete the formula.

Vibratory polishing was used to polish the various samples for a period of 24 hours. The polishing rate for each abrasive in microns/hr was then determined. The result of the vibratory polishing of the three samples are found in Table II below:

TABLE II

Polishing Media	Mechanochemical Polishing Rate (microns/hr)		
	Alumina	Silicon Nitride	Zirconia
Al_2O_3 + colloidal silica	0.045	0.163	0.173
Ce_2O_3 + colloidal silica	0.027	0.300	0.1875
Ce_2O_3	0.006	0.135	—
Fe_2O_3 + colloidal silica	0.125	0.300	0.448
Fe_2O_3	0.003	0.042	0.173
Cr_2O_3 + colloidal silica	0.148	0.188	0.233
Cr_2O_3	0.00	0.058	0.00
(CS) colloidal silica	0.044	—	0.058

The colloidal silica used above is the same colloidal silica used in the mechanochemical polishing abrasive. No water was added to the colloidal silica before it was used for testing purposes.

A slurry was made of each of the mechanical abrasives used in the testing by adding 5 ml of deionized water to about 20 g of the powdered mechanical abrasive.

Polishing pressures and temperatures were not critical to the results but were maintained as uniform throughout the testing as possible. The polishing temperature was held at about 25° C. while the polishing pressure was kept at about 50 gm/cm².

In most cases, the mechanochemical polishing abrasive of this invention polished each material at a higher rate than the colloidal silica or the mechanical abrasive alone or cumulatively. Only the Ce_2O_3 plus colloidal silica, polishing alumina, showed a lower polishing rate than colloidal silica alone.

What I claim is:

1. A method for polishing a workpiece with a mechanochemical polishing abrasive comprising a slurry of colloidal silica and one or more mechanical abrasives other than silica by applying the mechanochemical polishing abrasive to a workpiece and contacting the workpiece with a polishing means for a period of time sufficient to polish at least one surface of the workpiece, said workpiece comprising a surface which has normally greater hardness than said one or more mechanical abrasives present, said workpiece surface also being interactive with colloidal silica to be softened to permit abrasion of said softened workpiece surface by said one or more mechanical abrasives.

2. The polishing method of claim 1 further characterized in that the mechanochemical polishing abrasive is applied to the polishing means.

3. The polishing method of claim 1 further characterized in that the polishing means is a mechanical polishing means utilizing a polishing pad.

4. A method for polishing a workpiece with a mechanochemical polishing abrasive comprising an aqueous slurry of colloidal silica, and a mechanical abrasive of at least one of the materials selected from the group consisting of Fe_2O_3 , Fe_3O_4 , MgO , BaCO_3 , CaCO_3 , MnO_2 , CeO , SiO_2 , CeO_2 , Cr_2O_3 , and Al_2O_3 by applying the mechanochemical polishing abrasive to a pad located on a mechanical polishing means and frictionally contacting the pad of the mechanical polishing means with at least one surface of the workpiece for a period of time sufficient to polish the surface of the workpiece, said surface of said workpiece having a hardness which is greater in its normal condition than the hardness of said mechanical abrasive, said surface of the workpiece being interactive with colloidal silica to be softened thereby and to be abraded by said mechanical abrasive.

5. The method of 4 in which said mechanical abrasive has a particle size of about 0.1 micron to about 10 microns.

6. The method of claim 5 in which said colloidal silica has a pH greater than about 7.0.

7. The method of claim 6 in which said polishing abrasive comprises about 13 to about 99.2 weight percent of aqueous slurry of colloidal silica, from about 0.7 to about 85 weight percent of water, and from about 0.07 to about 2.0 weight percent of said mechanical abrasive.

8. The method of claim 6 in which said mechanical abrasive has a particle size from about 0.5 micron to about 5 microns.

9. The method of claim 5 in which said mechanical abrasive is selected from the group consisting of Al_2O_3 , Ce_2O_3 , Fe_2O_3 , and Cr_2O_3 .

10. The method of claim 9 in which said workpiece defines a surface made of a material selected from the group consisting of alumina, silicon nitride, and zirconia.

11. The method of claim 1 in which said workpiece defines a surface made of a material selected from the group consisting of alumina, silicon nitride, and zirconia.

12. The method of claim 1 in which said mechanical abrasive is selected from the group consisting of Al_2O_3 , Ce_2O_3 , Fe_2O_3 , and Cr_2O_3 .

13. The method of claim 12 in which said workpiece defines a surface made of a material selected from the group consisting of alumina, silicon nitride, and zirconia.

14. The method of claim 1 in which said colloidal silica has a pH greater than about 7.0.

15. The method of claim 1 in which the particle size of said mechanochemical polishing abrasive is larger than the particle size of said colloidal silica.

16. The method of claim 4 in which the particle size of said mechanochemical polishing abrasive is larger than the particle size of said colloidal silica.

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US005868604A

United States Patent [19]

Atsugi et al.

[11] Patent Number: 5,868,604

[45] Date of Patent: Feb. 9, 1999

[54] ABRASIVES COMPOSITION, SUBSTRATE AND PROCESS FOR PRODUCING THE SAME, AND MAGNETIC RECORDING MEDIUM AND PROCESS FOR PRODUCING THE SAME

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[51] Int. Cl.⁶ B05D 5/00; C01F 7/02; C09G 1/02; C23C 22/05

[52] U.S. Cl. 451/36; 51/309; 106/1.05

[58] Field of Search 51/307, 308, 309; 451/36; 427/355; 106/1.05, 286.5

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[57] ABSTRACT

An abrasives composition comprises (i) one or more abrasives, (ii) one or more abrasion accelerators and (iii) water. The abrasive comprises intermediate alumina particles having a mean particle size of primary particles of 40 nm or less.

13 Claims, 1 Drawing Sheet

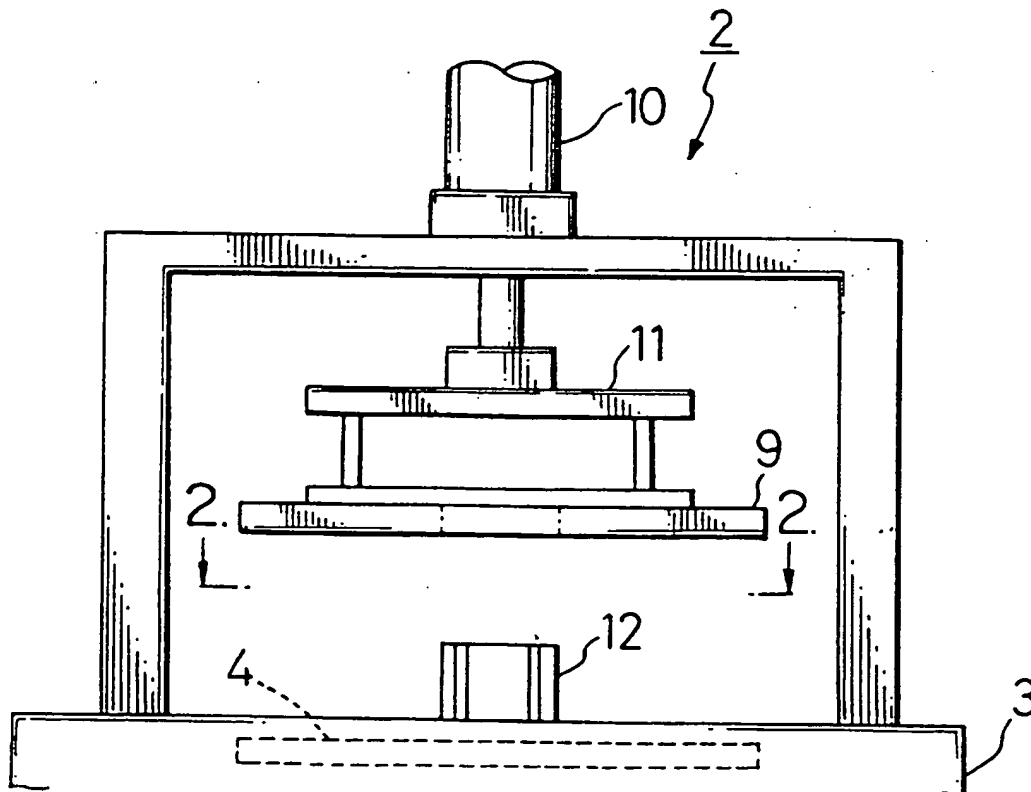


Fig. 1

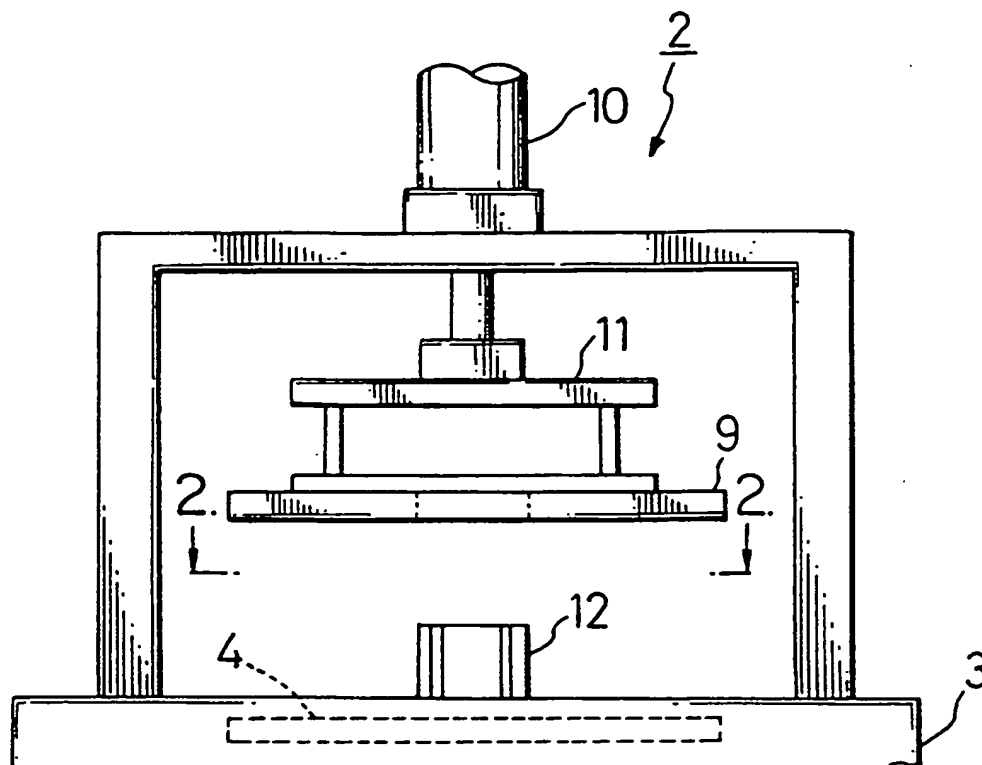
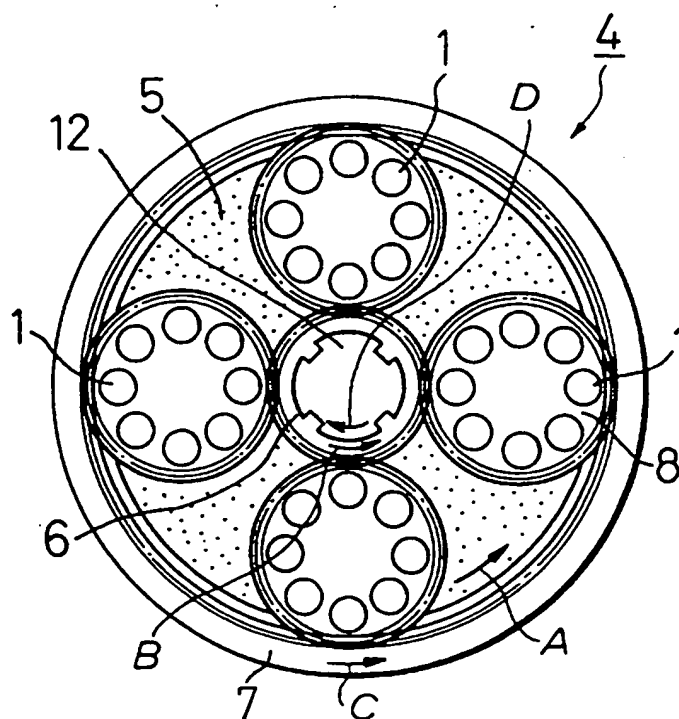


Fig. 2



ABRASIVES COMPOSITION, SUBSTRATE AND PROCESS FOR PRODUCING THE SAME, AND MAGNETIC RECORDING MEDIUM AND PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to an abrasives composition. This invention particularly relates to an abrasives composition capable of producing a substrate for a magnetic recording medium, which substrate has a very small value of surface roughness. This invention also relates to a process for producing a substrate, wherein the abrasives composition is used. This invention further relates to a glass-like carbon substrate for a magnetic recording medium, wherein the substrate has a very small value of surface roughness, and a magnetic recording medium using the glass-like carbon substrate.

2. Description of the Related Art

Recently, most computers are provided with recording devices, such as magnetic disk drives. With the increase in the amount of recorded information occurring in recent years, it is required that recording devices be capable of recording information at high densities. The magnetic disk drive has a magnetic head and a magnetic disk. As a means for achieving the recording of information at high densities, it is necessary to reduce the glide height of the magnetic head. For such purposes, it is necessary that the surface roughness (Ra) of the magnetic disk be as small as possible.

Recently, glass-like carbon substrates have attracted particular attention as substrates for magnetic disks. The glass-like carbon substrates have a hardness higher than aluminum substrates, which are currently popular as the substrates for magnetic disks. Therefore, the thickness of the substrates can be reduced when made of glass-like carbon. Also, glass-like carbon has a small specific gravity and is light in weight, and therefore glass-like carbon substrates are light in weight. Accordingly, substrates are very suitable for use in computers, which should be kept small in size and light in weight.

However, when glass-like carbon substrates are used as substrates for magnetic disks, it is difficult for the surface roughness of the glass-like carbon substrates to be reduced, due to the high hardness of the glass-like carbon. Specifically, if γ -alumina particles, typically used, are used in polishing step carried out during the production of the substrates for magnetic disks, the surface roughness of the substrates cannot be reduced (e.g., to less than 4 Å). This is because the α -alumina particles are hard and the mean particle size of their primary particles is at least 0.1 μ m. If very soft abrasive is used in lieu of α -alumina particles, sufficient abrasive effects cannot be obtained, and the surface roughness cannot be reduced.

Japanese Patent Application Laid-Open 7-240025 proposes a method for reducing the surface roughness of a magnetic disk substrate. The method comprises the step of corroding a substrate material with a chemical corrosive agent, which reacts with the substrate material and softens a portion of the substrate material, and the step of abrading and removing this portion of the substrate material using colloidal particles. Also proposed is a magnetic disk substrate having a surface roughness of less than 4 Å. However, it is difficult to reduce the surface roughness of a glass-like carbon substrate to less than 4 Å with the method proposed in this patent application.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an abrasives composition capable of imparting a low surface roughness to a substrate, particularly a glass-like carbon substrate, so that information can be recorded on the magnetic recording medium at high densities.

Another object of the present invention is to provide a substrate, in particular a substrate for a magnetic recording medium, having a very low surface roughness, and a process for producing the substrate.

The inventors carried out extensive research in order to achieve these objects and found that the surface of a substrate can be efficiently processed to the super-polished state by an abrasives composition containing specific alumina particles. The present invention is based on these findings.

The present invention provides an abrasives composition, comprising:

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water,

wherein the abrasives comprise intermediate alumina particles having a mean particle size of primary particles of 40 nm or less.

The present invention also provides a process for producing a substrate, comprising:

abrading surfaces of said substrate with an abrasives composition,

wherein said abrasives composition comprises

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water, and

said abrasives comprise an intermediate alumina particle having a mean particle size of primary particles of 40 nm or less.

The present invention further provides a substrate, comprising glass-like carbon, wherein said substrate has a surface roughness Ra of less than 4 Å.

The present invention still further provides a magnetic recording medium, comprising:

- (i) the above-mentioned glass-like carbon substrate,
- (ii) a magnetic layer on said substrate, and
- (iii) a protective layer on said magnetic layer.

With the abrasives composition in accordance with the present invention, wherein the abrasives comprise the intermediate alumina particles having a mean particle size of primary particles of 40 nm or less, a low surface roughness can be imparted to the substrate, so that information can be recorded on the magnetic recording medium at high densities.

In particular, with the abrasives composition in accordance with the present invention, high-hardness substrates, e.g. glass-like carbon substrates, for which the super-polishing process ordinarily cannot easily be carried out, can be processed such that the surface roughness of the abraded substrates may be less than 4 Å, providing very smooth surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic front view showing a double-sided polishing machine, which may be used in a polishing step for a substrate for a magnetic recording medium; and

FIG. 2 is a view taken along line X—X of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

Firstly, the abrasives composition in accordance with the present invention will be described in detail.

said range, appropriate oxidizing effects can be obtained. Therefore, the substrate can be processed efficiently to a desired low surface roughness (e.g., of less than 4 Å), and the production efficiency can be increased.

The abrasives composition in accordance with the present invention can be prepared by, for example, adding the intermediate alumina particle, the abrasion accelerator, and the other components which will be described later, into water under stirring.

The content of water in the abrasives composition in accordance with the present invention is preferably 40% to 99.9% by weight, and more preferably 85% to 99.5% by weight. When the content of water in the abrasives composition falls within the aforesaid range, the substrate can be processed efficiently to a desired low surface roughness (e.g., of less than 4 Å), and the production efficiency can be increased.

If necessary, components other than those described above may also be added to the abrasives composition in accordance with the present invention. Examples of such other components include a dispersing agent for the abrasive, and a dispersing agent for fine powders which occur as a result of abrasion. The content of these components in the abrasives composition is preferably 0.5% to 10% by weight.

The substrate to be abraded with the abrasives composition in accordance with the present invention is preferably a substrate for a magnetic recording medium, for example, a carbon substrate, in particular a glass-like carbon substrate. However, the type of the substrate is not limited thereto. For example, the abrasives composition in accordance with the present invention is also applicable to the abrasive processing of other substrates, e.g. a glass substrate such as a reinforced glass substrate and a glass ceramic, and an aluminum substrate.

When the abrasives composition in accordance with the present invention is used for the polishing process carried out on the substrate for a magnetic recording medium, an abraded substrate having a low surface roughness, which is necessary to satisfy the recent demand for recording information on a magnetic recording medium at high densities, can be obtained.

A preferred process for producing the substrate for a magnetic recording medium, in which the abrasive processing step is carried out with the abrasives composition in accordance with the present invention, will be described below with reference to FIGS. 1 and 2, by taking the super-polishing process of a glass-like carbon substrate as an example. FIG. 1 is a schematic front view showing a double-sided polishing machine, which may be used in a polishing step in the production of a substrate for a magnetic recording medium. FIG. 2 is a view taken along line X—X of FIG. 1.

With reference to FIGS. 1 and 2, a double-sided polishing machine 2 is provided with a base 3 and a lower lap 4, which is located on the base 3 and rotates in the direction indicated by the arrow A. A polishing pad 5 is fitted to the upper-surface of the lower lap 4.

As illustrated in FIG. 2, a plurality of planetary gear-like carriers 8 are located on the upper side of the lower lap 4. Each carrier 8 is engaged with a sun gear 6, which is located at the center of the lower lap 4 and rotates in the direction indicated by the arrow B, and an internal gear 7, which is located on the outer circumference of the lower lap 4 and rotates in the direction indicated by the arrow C. Thus each carrier 8 rotates around the sun gear 6 and around its own

axis. Each carrier 8 has a plurality of holes, and glass-like carbon substrates 1 serving as work pieces are respectively set in the holes.

Also, as illustrated in FIG. 1, an upper lap 9 is located above the lower lap 4 and the carriers 8. A polishing pad (not shown) is fitted to the lower surface of the upper lap 9. The upper lap 9 is rotatably mounted on a bracket 11, which is fitted to the end of the output rod of an air cylinder 10. The upper lap 9 can be moved up and down by the air cylinder 10. When the upper lap 9 is moved down, it is engaged with grooves of a rotor 12 on the base side. The rotor 12 rotates in the direction indicated by the arrow D in FIG. 2, and the associated upper lap 9 rotates in the same direction.

The abrasives composition in accordance with the present invention is supplied from a slurry feed pipe (not shown) to the position between the upper lap 9 and the lower lap 4.

When the upper lap 9 is moved down by the air cylinder 10, the glass-like carbon substrates 1, which move together with each carrier 8, are sandwiched between the lower lap 4 and the upper lap 9. In this manner, the abrasive processing is carried out.

In general, the super-polishing process of glass-like carbon substrates may be carried out with the aforesaid double-sided polishing machine under the conditions described below.

Specifically, the processing pressure is preferably 10 to 2,000 g/cm², and more preferably 30 to 1,500 g/cm².

The processing time is preferably 2 to 120 minutes, and more preferably 2 to 30 minutes.

The hardness [JIS A(JIS K-6301)] of the abrasion pads fitted to the platens of the double-sided polishing machine is preferably 40 to 100, and more preferably 60 to 100.

The rotation speed of the lower lap of the double-sided polishing machine may vary in accordance with the size of the polishing machine. For example, as for a 9B type double-sided polishing machine manufactured by SPEED FAM CO., the rotation speed of the lower lap is preferably 10 to 100 rpm, and more preferably 10 to 60 rpm.

The supplying rate of the abrasives composition may vary in accordance with the size of the polishing machine. For example, as for the 9B type double-face polishing machine manufactured by SPEED FAM CO., the supplying rate of the abrasives composition is preferably 5 to 300 cc/min, and more preferably 10 to 150 cc/min.

When the super-polishing process is carried out on glass-like carbon substrates, i.e. the abrasive processing is carried out on the surfaces of a glass-like carbon substrate, under the conditions described above, a glass-like carbon substrates, which are ordinarily difficult to process to smooth surfaces, can be processed to a surface roughness of less than 4 Å.

The preferred process for producing the substrate for a magnetic recording medium, in which the abrasive processing step is carried out with the abrasives composition in accordance with the present invention, has been described above. However, the production process is not limited to the embodiment described above and may be applied to, for example, substrates other than the glass-like carbon substrates. In addition, the abrasives composition of the present invention is advantageous for the production of substrates other than a substrate for a magnetic recording medium, for example, a silicon wafer and various lenses which require a low surface roughness.

In the present invention, the magnetic recording medium can be obtained by using the glass-like carbon substrate which has been obtained in the manner described above and

TABLE 1

	Type of Alumina	Particle Size* of Alumina (nm)	pH of Abrasives Composition	Aluminum Nitrate (wt %)	Surface Roughness (Å)	Number of Defects (pieces)
Examples	1 γ -Al ₂ O ₃	20	3.8	1	3.2	0
	2 γ -Al ₂ O ₃	40	3.8	1	3.9	0
	3 θ -Al ₂ O ₃	30	3.8	1	3.9	0
Comparative Examples	1 α -Al ₂ O ₃	1000	3.8	1	12.1	0
	2 γ -Al ₂ O ₃	40	7.2	0	15.0	>500
	3 γ -Al ₂ O ₃	45	3.8	1	5.3	120

*Mean particle size of primary particles

TABLE 2

		GHT
Examples	4	Very Good
	5	Very Good
	6	Very Good
Comparative Examples	4	Poor
	5	Poor
	6	Good

As is clear from the results shown in Table 1, when the super-polishing process was carried out on the glass-like carbon substrates using the abrasive compositions in accordance with the present invention (Examples 1, 2 and 3), no defect occurred on the surface of the abraded substrates, and the surface roughness of the abraded substrates could be reduced to a very small value (less than 4 Å). On the other hand, when α -alumina particles were used as the abrasive (Comparative Example 1), though no defect occurred, the low surface roughness obtainable with the abrasive composition in accordance with the present invention could not be obtained. Also, when the abrasive processing was carried out with an abrasives composition containing no abrasion accelerator (Comparative Example 2), many defects occurred on the surface of the abraded substrate, and the low surface roughness obtainable with the abrasive compositions in accordance with the present invention could not be obtained. Further, in cases where the abrasive processing was carried out with the abrasives composition containing the abrasive having a mean particle size larger than 40 nm (Comparative Example 3), defects occurred on the surface of the abraded substrate, and the low surface roughness obtainable with the abrasive compositions in accordance with the present invention could not be obtained.

Also, as is clear from the results shown in Table 2, the magnetic disks (Examples 4, 5 and 6) which use the glass-like carbon substrates (obtained in Examples 1, 2 and 3) subjected to the super-polishing process using the abrasive compositions in accordance with the present invention, had a low substrate surface roughness and exhibited good GHT results. On the other hand, the magnetic disks (Comparative Examples 4, 5 and 6) which use the substrates obtained in Comparative Examples 1, 2 and 3, exhibited GHT results inferior to those obtained with the magnetic disks of Examples 4, 5 and 6, because the magnetic disks in Comparative Examples 4, 5 and 6 do not use substrates having a surface roughness as low as obtained in Examples 1, 2 and 3.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teaching. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described therein.

15 The priority documents of the present application, Japanese Patent Applications No. 7-292567 and No. 8-71577, filed on Nov. 10, 1995 and Mar. 27, 1996, respectively, are hereby incorporated by reference.

What is claimed as new and is desired to be secured by Letters Patent of the United States is:

1. An abrasives composition, comprising:

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water,

wherein said abrasives consist essentially of intermediate alumina particles having a mean particle size of primary particles of 40 nm or less wherein said intermediate alumina particles comprise an abrasive effective amount of at least one member selected from the group consisting of γ -alumina and θ -alumina.

2. The abrasives composition of claim 1, wherein said abrasives composition has a pH of 5 or less.

3. The abrasives composition of claim 1, wherein said abrasion accelerator comprises at least one metal salt containing an oxidizing group.

4. The abrasives composition of claim 1, wherein said intermediate alumina particles have a means particle size of primary particles of 10 to 40 nm.

5. The abrasives composition of claim 1, comprising:

- 40 to 99.9% by weight of said water,
- 0.05 to 30% by weight of said abrasion accelerator, and
- 0.05 to 30% by weight of said intermediate alumina particles.

6. The composition according to claim 1, wherein said intermediate alumina particles comprise γ -alumina.

7. An abrasives composition, prepared by mixing 40 to 99.9% by weight of water,

- 0.05 to 30% by weight of at least one abrasion accelerator, and

0.05 to 30% by weight of, one or more abrasives, wherein said abrasives consist essentially of intermediate alumina particles having a mean particle size of primary particles of 40 nm or less and comprise an abrasive effective amount of at least one member selected from the group consisting of γ -alumina and θ -alumina.

8. The abrasives composition of claim 7, wherein said intermediate alumina particle comprises γ -alumina.

9. A process for producing a substrate, comprising:

- abrading a surface of said substrate with an abrasives composition.

United States Patent [19]
Rosenblum

[11] 4,021,263
[45] May 3, 1977

[54] POLISHING COMPOSITIONS

- [75] Inventor: Marc Rosenblum, Milltown, N.J.
[73] Assignee: Johnson & Johnson, New Brunswick, N.J.
[22] Filed: Feb. 27, 1975
[21] Appl. No.: 553,704

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 214,719, Jan. 3, 1972, abandoned.
[52] U.S. Cl. 106/288 B; 51/307; 51/309 A
[51] Int. Cl.² C09G 1/02
[58] Field of Search 106/288 B, 308 B; 51/307, 309; 423/446

[56]

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[57]

ABSTRACT

Polishing compositions for highly filled resin-bonded dental restorations comprising a dispersion of alumina having a particle size less than about 3.0 microns and for nonprecious metal used in dental construction comprising a dispersion of said alumina and diamond having a particle size at least equal to that of the alumina but less than about 3.0 microns.

4 Claims, No Drawings

POLISHING COMPOSITIONS

REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my co-pending application, Ser. No. 214,719 filed Jan. 3, 1972, now abandoned.

BACKGROUND OF THE INVENTION

The present invention pertains to polishing compositions, and more particularly to polishing compositions for highly-filled resin-bonded dental restorations and nonprecious metal used in dental construction.

Materials used in dental restorations and dental construction must be polished in order to be acceptable to the dentist and the patient. Polished materials have a finished appearance and a smooth, natural feel in the mouth. Moreover, polished materials collect plaque less readily than unpolished materials and hence need cleaning less often. For these reasons it is desirable that materials used in dental restoration be polished. This polishing is generally accomplished in three steps, using successively finer abrading agents. The compositions of the invention are designed for use in the final polishing step, after the surface has been roughly finished and then prepared for polishing. The rough finishing may be accomplished with a number of commonly-available abrasive silicon carbide greenstones or carbide burrs as is well-known in the dental art. The second step, the finishing preparatory to polishing, may be accomplished with a number of commonly-available abrasive fine aluminum oxide whiteners and fine rubber-bound abrasive tools (e.g. a Dedco Tan Midget) as is well-known in the dental art.

Both highly-filled resin-bonded dental restorations and nonprecious metal dental constructions comprise a harder phase and a softer phase. In the former material, the quartz or other filler is much harder than the resin bonding agent; in the latter material, as disclosed for example in United States patent application Ser. No. 376,767, filed July 5, 1973, the nickel boride-chromium silicide included phase is harder than the surrounding nickel chromium matrix. Using prior art polishing compositions generally results in a more rapid abrading of the softer phase than of the harder phase to produce a "stepped" effect. That is, the resin is gouged out from between the quartz particle or the matrix is worn away more rapidly than the included phase. The resulting uneven surface is not polished. In order to have effective polishing there must be substantially equal abrasion of both phases of the material so that a smooth, even surface is produced.

Further, it is necessary to have efficient polishing, so that a dental technician or dentist can rapidly polish a nonprecious metal dental construction or a highly-filled resin-bonded dental restoration. Certain prior art pastes for polishing the former have been relatively effective polishing agents without being satisfactorily efficient. These pastes are unsatisfactory when compared with the pastes of the invention. It is also clear that the use of two or more pastes in the final polishing step is highly unsatisfactory because of the excessive amount of time necessary to polish using them.

The disadvantages of the prior art polishing compositions are obviated by the compositions of the present invention.

SUMMARY OF THE INVENTION

The present invention provides a polishing composition capable of effectively and efficiently polishing highly-filled resin-bonded dental restorations, which composition comprises a dispersion of finely divided alumina in an inert and biologically safe solvent. The present invention further provides a polishing composition capable of effectively and efficiently polishing nonprecious metal dental constructions which composition comprises a dispersion of finely divided alumina and finely divided diamond in an inert and biologically safe solvent.

The compositions of the invention are superior to those of the prior art because they efficiently provide a smooth, polished, non-stepped surface on the dental restoration or dental constructions, in contrast to that provided by polishing compositions of the prior art.

DETAILED DESCRIPTION OF THE INVENTION

First consider the composition for polishing highly-filled resin-bonded dental restorations. In this composition, the alumina should have a particle size of less than about 3.0 microns, preferably from about 0.05 microns to about 2.0 microns, and more preferably from about 0.3 microns to about 1.0 microns; and should be present in a concentration from about 5% to about 50% by weight, preferably from about 20% to about 40% and more preferably from about 25% to about 35% by weight of the weight of the dispersion. The remainder of the composition comprises essentially the inert and biologically safe carrier such as, for example, water, glycerol, sorbitol, polyethylene glycol, and the like. This composition may have a viscosity from about 600 cps to about 40,000 cps, but preferably from about 1200 cps to about 40,000 cps, and more preferably from about 3000 cps to about 10,000 cps. It is considered to be within the scope of the present invention to add dye, flavoring, preservative, or the like to the polishing composition. A suspension agent may also be added to prevent settling of the alumina during storage of the paste. Such a suspension agent may be, for example, submicron silica or the like inert and biologically safe hydrophobic colloid. A preferred submicron silica is that sold by Degussa Company under the trade name Aerosil R-972. The composition containing submicron silica has a viscosity of from about 1 million cps to about 3 million cps. Using this composition of the invention, highly-filled resin-bonded dental restorations can be effectively and efficiently polished.

Next consider the composition for polishing nonprecious metal dental constructions. In this composition, the diamond should have a particle size less than about 3.0 microns, preferably from about 0.05 microns to about 1.0 microns, and more preferably about 0.25 microns. The alumina should have a particle size less than about 3.0 microns, preferably from about 0.05 microns to about 1.0 microns, and more preferably about 0.05 microns; provided that the particle size of the diamond should be at least equal to that of the alumina. The diamond should be present in a concentration of from about 0.25% to about 25.0% by weight, preferably from about 0.25% to about 5.0% by weight, and more preferably about 0.50% by weight of the weight of the composition. The alumina should be present in a concentration of from about 15% to about 50% by weight, preferably from about 20% to about 40% by weight, and more preferably about 40% by

weight of the weight of the composition. The remainder of the composition comprises essentially an inert and biologically safe carrier such as, for example, water, glycerol, sorbitol, polyethylene glycol, silicone grease, petrolatum, and the like. It is considered to be within the scope of the present invention to add coloring, perfume, preservatives, or the like to the polishing composition. Using this composition of the invention, nonprecious metal dental constructions can be effectively and efficiently polished.

While it is recognized that the polishing achieved by the diamond and alumina composition of the present invention could also be achieved by polishing the nonprecious metal dental constructions either with diamond alone or first with alumina and then with diamond, this procedure would not yield the rapid and effective polishing achieved by the composition of the invention. Using a polishing paste containing only diamond results in less efficient polishing, which is more time-consuming than the use of the composition of the invention and hence undesirable. Using two separate polishing pastes for the final polishing step is even more wasteful of time and hence even more undesirable. Only by using the diamond and alumina polishing composition of the present invention can a dental technician polish nonprecious metal dental construction in an effective and efficient fashion.

The preferred tool for polishing a highly-filled resin-bonded dental restoration or a nonprecious metal dental construction with the compositions of the invention is one of felt, as for example a felt wheel or a felt tip.

The compositions of the invention are illustrated by the following examples, which are intended only for purposes of illustration and not to limit the scope thereof. All parts are by weight unless otherwise specified.

EXAMPLE I

A polishing composition is prepared comprising the following:

1.0 micron alumina	19.0 parts
0.3 micron alumina	4.0 parts
0.05 micron alumina	2.0 parts
glycerol	75.0 parts
Total	100.0 parts

These ingredients are mixed in a ball-mill for one half hour and then are tested. This composition effectively and efficiently polishes a highly-filled resin-bonded dental restoration.

EXAMPLE II

A polishing composition is prepared which comprises the following:

0.05 micron alumina	39.5 grams
0.25 micron diamond	0.5 grams
polyethylene glycol 400	60.0 grams
Total	100.0 grams

The components of the composition are thoroughly mixed and the composition is tested. This combination efficiently and effectively polishes a nonprecious metal dental construction.

EXAMPLE III

Following the procedure of Example I, polishing compositions are prepared which comprise:

a)	1.0 micron alumina	25 parts
	glycerol	75 parts
b)	1.0 micron alumina	50 parts
	glycerol	50 parts
c)	3.0 micron alumina	5 parts
	glycerol	95 parts
d)	0.3 micron alumina	15 parts
	water	85 parts
e)	2.0 micron alumina	10 parts
	sorbitol	90 parts
f)	1.0 micron alumina	30 parts
	glycerol	67 parts
	submicron silica	3 parts

These compositions all effectively and efficiently polish highly-filled resin-bonded dental restorations.

EXAMPLE IV

Following the procedure of Example II, polishing compositions are prepared comprising:

a)	1.0 micron alumina	39 parts
	1.0 micron diamond	1 part
	polyethylene glycol 400	60 parts
b)	0.3 micron alumina	15 parts
	1.0 micron diamond	0.5 parts
	petrolatum	84.5 parts
c)	0.05 micron alumina	50 parts
	0.25 micron diamond	1 part
	polyethylene glycol 400	49 parts

These compositions all effectively and efficiently polish nonprecious metal dental constructions.

What is claimed is:

1. A polishing composition consisting essentially of:
 - a. from about 15% to about 50% of the weight of the composition alumina, said alumina having a particle size of less than about 3.0 microns;
 - b. from about 0.25% to about 25.0% by weight of the weight of the composition diamond, said diamond having a particle size less than about 3.0 microns but at least equal to that of the alumina; and
 - c. an inert, biologically safe, flowable carrier.
2. A composition as in claim 1 wherein the particle size of said alumina is from about 0.05 microns to about 1.0 microns and which comprises about 0.50% by weight diamond, said diamond having a particle size from about 0.05 microns to about 1.0 microns but said particle size being at least equal to that of said alumina.
3. A composition as in claim 2 wherein the particle size of said diamond is about 0.25 microns and wherein the particle size of said alumina is about 0.05 microns.
4. The composition of claim 1 wherein the inert, biologically safe, flowable carrier is a member selected from the group consisting of water, glycerol, sorbitol, polyethylene glycol, silicone grease, and petrolatum.

[54] ABRASIVE PARTICLE, METHOD FOR PRODUCING THE SAME, AND METHOD OF USE OF THE SAME

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05220394A 8/1993 Japan .
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[51] Int. CL⁶ C09C 1/68

[52] U.S. CL. 51/307; 51/309

[58] Field of Search 51/307, 309

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[57] ABSTRACT

Disclosed is an abrasive particle having an average particle size of not more than 2 μ m and comprising 100 parts by weight of aluminum oxide and/or silicon oxide and 5 to 25 parts by weight of cerium in the form of cerium oxide. A method for producing the same, and a method for planarizing an insulating film on a semiconductor substrate using the abrasive particles are also disclosed.

17 Claims, No Drawings

1 ABRASIVE PARTICLE, METHOD FOR PRODUCING THE SAME, AND METHOD OF USE OF THE SAME

FIELD OF THE INVENTION

The present invention relates to an abrasive particle, a method for producing the same, and a method for planarizing an insulating film formed on a semiconductor substrate, which comprises planarizing the insulating film formed on the semiconductor substrate, using the abrasive particles.

BACKGROUND OF THE INVENTION

With the rapid progress of the LSI technology, an integrated circuit has been liable to become fine and form multilayer interconnection more and more. The multilayer interconnection in an integrated circuit drastically increases any problems associated with any irregularities in the semiconductor surface, and the presence of any difference in levels due to an irregularity causes breaks in the printing at the uneven levels and local increases in resistance. The presence of level differences in fine integrated circuits tends to cause wires to break, decreases in current capacity, and decreases in electromigration, etc., which results in yield decreases and inferior reliability.

Therefore, it has been desired to develop a technique for planarizing interlayer dielectrics of SiO_2 , which insulates between an element or printing of the lower layer and a wiring of the upper layer in a multilayer interconnection substrate, in order to eliminate any irregularity between the respective layers.

Various conventional planarizing techniques have been suggested. When a method of reflow or etch back of SOG (spin-on-glass; application glass method) is applied to a device having a wiring width of not more than $0.35 \mu\text{m}$, it is difficult to planarize the whole device. Therefore, a CMP (Chemical Mechanical Polishing) method which makes it possible to planarize the whole device has been drawing special interest.

In the planarizing step of the insulating film of the semiconductor according to this CMP method, a slurry prepared by dispersing colloidal silica or fumed silica in an aqueous alkaline solution of KOH, NaOH, etc. has hitherto been used as the polishing agent. When silica is used as the polishing agent for the SiO_2 insulating film, defects do not arise. However, a sufficient polishing rate cannot be obtained by merely dispersing the colloidal silica or fumed silica in water because the polishing agent and the insulating film to be polished are the same material. Accordingly, the polishing rate has been improved by combining the above aqueous alkaline solution with the polishing agent. However, another problem arises such that, when the insulating film is polished using a polishing agent slurry containing the alkaline metal, the alkaline metal in the slurry diffuses into the insulating film to drastically deteriorate the reliability of the semiconductor device.

As a method for solving the above problem, a method of using a polishing agent containing cerium oxide has been disclosed (Japanese Patent Kokai (Laid-Open) No. 5-326469). It is described that, when the insulating film on the semiconductor substrate is polished by this method, it can be polished at high speed without using an alkaline metal solution.

However, the cerium oxide is normally produced from a ore such as a bastnaesite ore via pulverization, classification, calcination, etc. and, therefore, the particle size is uneven in

comparison with an artificial oxide and the reproductivity and stability of the polishing ability are inferior. Further, the bastnaesite ore has low purity and normally contains α ray radioactive elements as impurities because it is natural ore. Therefore, when the polishing agent adheres and remains on the device, soft errors due to α ray radiation are liable to arise. High-purity cerium oxide without such impurities is very expensive and it is difficult to industrially apply high-purity cerium oxide as the polishing agent because of the cost.

As another polishing agent for a metal or glass surface, aluminum oxide has hitherto been known. Aluminum oxide has a high hardness and is cheaper than high-purity cerium oxide and, therefore, it is a substance which has widely been used as a polishing agent. Regarding polishing of the semiconductor insulating film using it, however, the polishing rate is low and defects such as scratches, orange peels, etc. are formed on the polished surface. Therefore, it cannot be put to practical use.

The present inventors have studied the above issues in order to discover a polishing agent which is suitable for planarizing an insulating film on a semiconductor substrate, which is inexpensive, which provides for a high polishing rate without using a solution of an alkaline metal, which causes few defects (e.g., scratches, orange peels, etc.), and which avoids α ray radiation that can cause soft errors. As a result, it has been found that an abrasive particle comprising aluminum oxide and/or silicon oxide and specific amount of cerium oxide and having a specific particle size range satisfies all of the above objects when such an abrasive particle is employed as a polishing agent for an insulating film on a semiconductor substrate. Thus, the present invention has been accomplished.

SUMMARY OF THE INVENTION

The present invention provides an abrasive particle which has an average particle size of $2 \mu\text{m}$ or less, and which comprises (a) 100 parts by weight of a metal oxide selected from aluminum oxide and silicon oxide and (b) 5 to 25 parts by weight of cerium in the form of cerium oxide.

The present invention also provides a method for producing the abrasive particles, which comprises a step of suspending in a solvent a compound selected from the metal oxide having an average particle size of $2 \mu\text{m}$ or less in an amount of 100 parts by weight and a precursor thereof which is converted by calcining to the metal oxide having an average particle size of $2 \mu\text{m}$ or less in an amount of 100 parts by weight to form a suspension; a step of mixing into the suspension a cerium compound which is converted by calcining to cerium oxide in an amount of 5 to 25 parts by weight in terms of cerium to form a mixture; a step of drying the mixture; and a step of calcining the dried mixture.

The present invention further provides a method for planarizing an insulating film on a semiconductor substrate, which comprises polishing the insulating film formed on the semiconductor substrate using a polishing agent which comprises the abrasive particles.

DETAILED DESCRIPTION OF THE INVENTION

The abrasive particle of the present invention comprises metal oxide selected from aluminum oxide and silicon oxide and cerium oxide, and is used as a polishing agent for, for example, an insulating film formed on a semiconductor substrate. The abrasive particle has an average particle size (average secondary particle size) measured by a light scat-

but the rotary kiln, tunnel furnace and shuttle furnace are normally suitable in view of productivity, heat resistance of materials, etc.

The surface appearance of the abrasive particle obtained by the above method was observed by a transmission electron microscope. As a result, the abrasive particle shows either a condition where the metal oxide surface is coated with the cerium oxide, a condition where a part of the metal oxide surface is coated with the cerium oxide or a condition where cerium oxide is included in the particle. The particles are not a mere mixture of the metal oxide powder and cerium oxide powder.

The abrasive particles thus obtained are normally used as a polishing agent, especially a wet polishing agent for planarizing the semiconductor insulating film in a form of a slurry dispersed into water.

Examples of the dispersing methods for converting the particles into a slurry include dispersing methods using a homogenizer, ultrasonic wave, wet medium mill, etc.

The slurry concentration is not specifically limited, and is normally about 2 to 30% by weight.

If necessary, known additives such as a dispersant, a suspension stabilizer and a defoamer can also be added to the polishing agent.

Examples of the semiconductor insulating film which is to be polished are known insulating films such as a thermally oxidized film, CVD film, spatter film, SOG film and fluorine-containing insulating film.

The abrasive particle of the present invention comprising inexpensive metal oxide, a specific amount of cerium oxide and having a specific particle size range exhibits high polishing performance without requiring an alkaline metal (e.g. NaOH, KOH, etc.) and causes few defects (e.g. scratches, orange peels, etc.) and emit little α ray radiation which can cause soft errors. Therefore, its utility value as a polishing agent for glass of photomask, glass substrate for liquid crystal or hard disc, etc. as well as polishing agent for polishing the insulating film on the semiconductor substrate is extremely significant. The abrasive particles can be obtained by a simple method.

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

The measurement in the Examples and Comparative Examples was conducted by the following method.

Average particle size (secondary): A particle size at 50% cumulation was measured by a Microtrack MKII particle size analyzer (SPA model 7997-20, manufactured by Nikkiso Co., Ltd.).

Radiation dose of α ray: It was measured by an α ray measuring device (Model ZDS-451, manufactured by Aloca Co.) when the radiation dose of α ray is 0.1 c/cm²-hr or more. It was measured by a low-level α ray measuring device (Model LACS-4000M, manufactured by Sumitomo Chemical Industries Co., Ltd.) when the radiation dose of α ray is less than 0.1 c/cm²-hr.

BET specific surface area: It was measured by a flow type specific area automatic measuring device (Model Flow Sorb II 2300PC-1A, manufactured by Shimadzu Corporation).

Content of Na and K: It was measured by Spark Source Mass Spectrometer (JEOL JMS-01BM-2).

EXAMPLE 1

To a slurry prepared by suspending 250 g of aluminum hydroxide having an average particle size of 0.6 μ m pro-

duced by hydrolysis of aluminum alkoxide in 940 ml of isopropyl alcohol (hereinafter referred to as IPA), a solution prepared by dissolving 52.69 g (amount corresponding to 10% by weight in terms of Ce based on aluminum oxide) of cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] in 170 g of IPA was added dropwise, followed by mixing with stirring. The mixed solution was heated at with refluxing for 2 hours and then dried by removing the solvent.

The dried mixture was calcined at 1050° C. for 3 hours. The resulting particles were examined by X-ray diffraction. As a result, the crystal form of aluminum oxide in the particles was γ -alumina. The average particle size, BET specific surface area and total content of Na and K were 0.8 μ m, 56 m²/g and 13 ppm, respectively. It has been confirmed by the results of the elemental analysis by transmission electron microscope (TEM-EDX) that cerium is contained in the respective primary particles of alumina.

The particles (30 g) thus obtained was dispersed in water (270 g) to form a slurry having a concentration of 10% by weight. Ammonium polycarboxylate (manufactured by San Nopco Limited) as the dispersant was added to this slurry in an amount of 0.5% by weight based on the particles to form a polishing agent slurry (pH: 9.3), and then a silicon oxide film having a film thickness of 1 μ m was polished. The polishing conditions are as follows: processing pressure: 110 g/cm², platen speed: 140 rpm and polishing pad: Rodel SUBA800 (trade name, manufactured by Rodel Co.). The polishing rate, state of surface defects and radiation dose of α ray were examined. The results are shown in Table 1.

EXAMPLE 2

According to the same manner as that described in Example 1 except for using an aqueous KOH solution as the dispersant of a polishing agent slurry in place of ammonium polycarboxylate and adjusting the pH to 10, a polishing agent slurry was obtained. A silicon oxide film was polished under the same condition as that of Example 1, using the resulting polishing agent slurry. The results are shown in Table 1.

EXAMPLE 3

According to the same manner as that described in Example 1 except for changing the amount of cerium nitrate to 105.38 g (amount corresponding to 20% by weight in terms of Ce based on aluminum oxide), abrasive particles were obtained. The crystal form of the aluminum oxide in the abrasive particles was γ -alumina. The average particle size, BET specific surface area and total content of Na and K were 0.8 μ m, 51 m²/g and 4 ppm, respectively.

According to the same manner as that described in Example 2, a polishing agent slurry was obtained from the resulting abrasive particles. A silicon oxide film was polished under the same condition as that of Example 1, using the resulting polishing agent slurry. The results are shown in Table 1.

EXAMPLE 4

According to the same manner as that described in Example 1 except for using 170 g of silicon oxide having an average particle size of 0.4 μ m in place of aluminum hydroxide having an average particle size of 0.6 μ m, abrasive particles were obtained. The average particle size, BET specific surface area and total content of Na and K of the particles were 0.6 μ m, 60 m²/g and 19 ppm, respectively.

According to the same manner as that described in Example 2, a polishing agent slurry was obtained from the

COMPARATIVE EXAMPLE 7

A silicon oxide film was polished under the same condition as that of Example 6, using the same slurry as that of Comparative Example 4. The results are shown in Table 2.

TABLE 2

	Polishing rate ²⁾ (Å/minute)	Surface appearance
Example 6	3540	No defect
Comparative Example 7	1160	No defect

²⁾ The polishing rate was calculated based on decrease in thickness of the film polished.

What is claimed is:

1. An abrasive particle which has an average particle size of 2 μm or less, and which comprises (a) 100 parts by weight of at least one metal oxide selected from the group consisting of aluminum oxide and silicon oxide and (b) 5 to 25 parts by weight of cerium as cerium oxide.

2. The abrasive particle according to claim 1, wherein said particle has a BET specific surface area of from 40 to 150 m^2/g .

3. The abrasive particle according to claim 1, wherein the metal oxide is aluminum oxide and the aluminum oxide is transition alumina.

4. The abrasive particle according to claim 1, wherein said abrasive particle has an impurity content of Na and K of 50 ppm or less.

5. The abrasive particle according to claim 1, wherein the particle is obtained by a method comprising a step of suspending in a solvent a compound selected from the metal oxide having an average particle size of 2 μm or less and a precursor thereof which is converted by calcining to the metal oxide having an average particle size of 2 μm or less to form a suspension; a step of mixing into the suspension a cerium compound which is converted by calcining to cerium oxide to form a mixture; a step of drying the mixture; and a step of calcining the dried mixture.

6. A method for producing abrasive particles, which comprises a step of suspending in a solvent at least one compound selected from the group consisting of aluminum oxide having an average particle size of 2 μm or less in an amount of 100 parts by weight, silicon oxide having an average particle size of 2 μm or less in an amount of 100 parts by weight and precursor aluminum or silicon oxide which is converted by calcining to aluminum oxide or silicon oxide having an average particle size of 2 μm or less in an amount of 100 parts by weight to form a suspension; a step of mixing into the suspension a cerium compound in an amount of 5 to 25 parts by weight in terms of cerium, wherein the cerium compound is converted to cerium oxide by calcining to form a mixture; a step of drying the mixture; and a step of calcining the dried mixture to obtain the abrasive particles having an average particle size of 2 μm or less, each of which comprises (a) 100 parts by weight of at least one metal oxide selected from the group consisting of aluminum oxide and silicon oxide and (b) 5 to 25 parts by weight of cerium as cerium oxide.

7. The method according to claim 6, wherein the cerium compound is at least one member selected from the group consisting of cerium nitrate, cerium acetate, cerium sulfate, cerium chloride, cerium oxalate, cerium carbonate, ammonium cerium sulfate and ammonium cerium nitrate.

8. The method according to claim 6, wherein aluminum oxide is obtained by hydrolysis of an organic aluminum compound.

9. The method according to claim 8, wherein the organic aluminum compound is an aluminum alkoxide.

10. The method according to claim 6, wherein the precursor of aluminum oxide is aluminum hydroxide obtained by hydrolysis of an organic aluminum compound.

11. The method according to claim 10, wherein the organic aluminum compound is an aluminum alkoxide.

12. The method according to claim 6, wherein the step of drying is carried out by a method using a flash drier or a pneumatic conveying drier.

13. A method for planarizing an insulating film on a semiconductor substrate, which comprises polishing the insulating film formed on the semiconductor substrate using a polishing agent which comprises abrasive particles having an average particle size of 2 μm or less, and each of the abrasive particles comprising (a) 100 parts by weight of at least a metal oxide selected from the group consisting of aluminum oxide and silicon oxide and (b) 5 to 25 parts by weight of cerium in the form of cerium oxide.

14. The abrasive particle according to claim 1, wherein said average particle size is about 0.2 μm to 1.0 μm .

15. The abrasive particle according to claim 2, wherein the BET specific surface area is from 40 to 100 m^2/g .

16. The abrasive particle according to claim 2, wherein the BET specific surface area is from 40 to 70 m^2/g .

17. A method for producing abrasive particles, which comprises a step of suspending in a solvent at least one compound selected from the group consisting of aluminum oxide having an average particle size of 2 μm or less in an amount of 100 parts by weight, silicon oxide having an average particle size of 2 μm or less in an amount of 100 parts by weight and precursor aluminum or silicon oxide which is converted by calcining at a temperature of from 600° C. to 1100° C. to aluminum oxide or silicon oxide having an average particle size of 2 μm or less in an amount of 100 parts by weight to form a suspension; a step of mixing into the suspension a cerium compound in an amount of 5 to 25 parts by weight in terms of cerium, wherein the cerium compound is converted to cerium oxide by calcining to form a mixture; a step of drying the mixture; and a step of calcining the dried mixture to obtain the abrasive particles having an average particle size of 2 μm or less, each of which comprises (a) 100 parts by weight of at least one metal oxide selected from the group consisting of aluminum oxide and silicon oxide and (b) 5 to 25 parts by weight of cerium as cerium oxide, wherein said aluminum oxide is a transition alumina mainly containing γ -alumina.

* * * * *

United States Patent [19]

Sakatani et al.

[11] Patent Number: 5,804,513

[45] Date of Patent: Sep. 8, 1998

[54] ABRASIVE COMPOSITION AND USE OF THE SAME

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[22] Filed: Aug. 29, 1997

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[52] U.S. Cl. 438/693; 51/308; 51/309; 106/3; 216/89

[58] Field of Search 106/3; 51/308; 51/309; 252/79.1; 438/692; 693; 216/89

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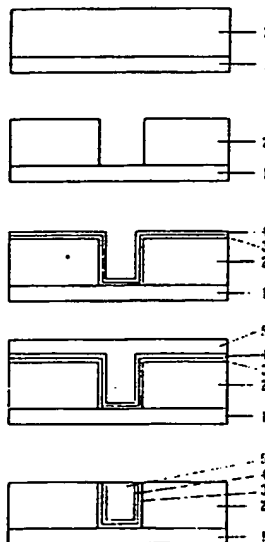
Primary Examiner—Deborah Jones

Attorney, Agent, or Firm—Birch, Stewart, Kolasch & Birch, LLP

[57] ABSTRACT

An abrasive composition is provided comprising an oxidizing agent and abrasive particles which have a mean particle size of 2 μ m or less, wherein each of the abrasive particles comprises (i) at least one oxide selected from aluminum oxide and silicon oxide and (ii) cerium oxide in an amount of 5% to 40% by weight in terms of cerium based on the oxide (i). A method for polishing and planarizing a metal layer formed on a semiconductor substrate using the abrasive composition is also provided.

14 Claims, 2 Drawing Sheets



1. a semiconductor substrate
 2. an insulating layer
 3. a metal contact layer
 4. an adhesion layer
 5. a metal layer for wiring

FIG 1 polishing apparatus using the CMP method

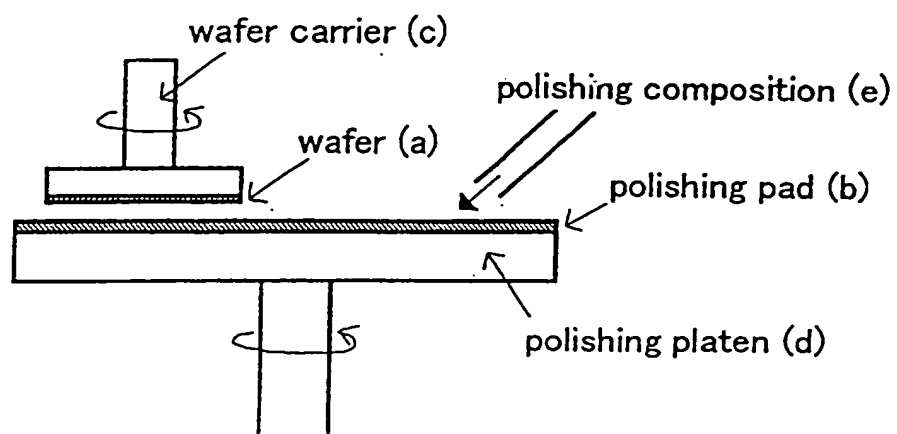


FIG 2(A)

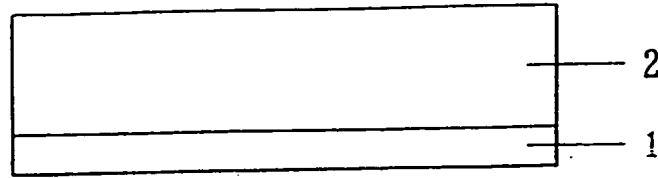


FIG 2(B)

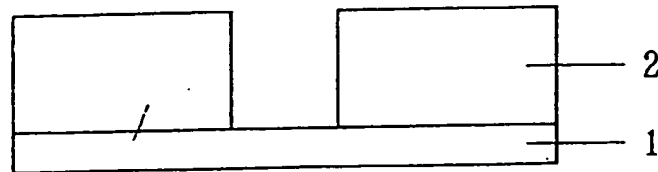


FIG 2(C)

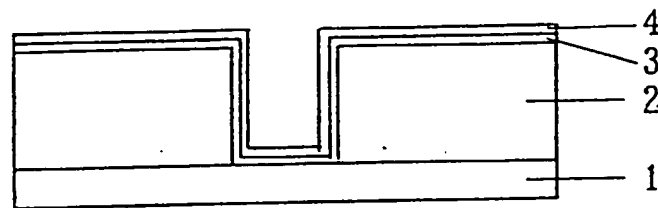


FIG 2(D)

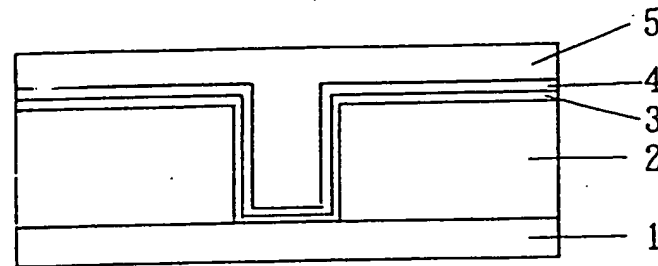
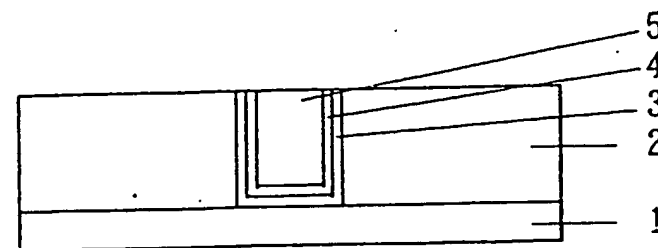


FIG 2(E)



1. a semiconductor substrate
2. an insulating layer
3. a metal contact layer
4. an adhesion layer
5. a metal layer for wiring

ABRASIVE COMPOSITION AND USE OF THE SAME

FIELD OF THE INVENTION

The present invention relates to an abrasive composition, a method of polishing and planarizing a metal layer formed on a semiconductor substrate using the abrasive composition.

BACKGROUND OF THE INVENTION

With extensive development of LSI techniques, integrated circuits have further been micronized and multilayer interconnected circuits have been frequently made. The multilayer interconnection of an integrated circuit enlarges unevenness on the surface of a semiconductor and the presence of the unevenness causes breaks in the printing and local increases in the resistance. And further in conjunction with the micronization of integrated circuits, the presence of the unevenness brings about a wire breaking, current capacity decrease and an occurrence of electromigration.

Therefore, a planarizing technique which planarizes a metal wiring and an interlayer insulating layer of a multilayer interconnected substrate and which decreases an unevenness between layers is required. Various planarizing processing techniques have been developed, and one of them is a chemical mechanical polishing technique (CMP method). This technique is used for the planarizing of an interlayer insulating layer, the formation of embedded wirings in the board and plug formation in production of semiconductors.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a schematic view of a polishing apparatus using the CMP method.

FIG. 2(A)-(E) are sectional views showing metal wiring parts.

FIG. 1 shows a schematic view of a polishing apparatus using the CMP method. The polishing is conducted as follows. That is, usually, a flat wafer (a) comprising a semiconductor material is kept on a wafer carrier (c) while introducing constant suction to the wafer carrier (c) in order to keep the wafer (a) attached to the wafer carrier (c). And a polishing platen (d) which supports a polishing pad (b) and the wafer carrier (c) which supports the wafer (a) are respectively rotated in the same directions as shown by the arrows for conducting the polishing. In this process, protruding parts of the insulating layer and the wiring are polished and planarized by a polishing composition introduced between the wafer and polishing pad. The properties of materials and additives in the polishing composition and the particle size of the abrasive particles in the polishing composition exert serious influence on the polishing rate and surface condition of the polished surface.

FIG. 2 shows one example for forming an embedded metal wiring board using the CMP method. FIG. 2 (A) to (E) are all sectional views and show only metal wiring parts.

First, as shown in Fig (A), an insulating layer 2 is formed on a semiconductor substrate 1 such as a silicon substrate, and the resulting insulating layer 2 is polished and planarized using an abrasive composition. A composition obtained by mixing a colloidal silica with an alkaline component such as potassium hydroxide or a composition containing cerium oxide is usually used as the abrasive composition for an insulating layer.

As shown in FIG. 2 (B), slits for metal wiring or openings for connecting wiring are formed in the insulating layer 2 by a photolithography method and etching method.

Next, as shown in FIG. 2 (C), a 'metal contact layer' 3 such as a titanium layer and an adhesion layer 4 such as a titanium nitride layer are formed on the slits or openings in the insulating layer 2 by methods such as sputtering, or a chemical vapor deposition (CVD) method, so that no mutual diffusion or reaction occur between the insulating layer 2 and 'metal layer for wiring' 5.

Next, as shown in FIG. 2 (D), the 'metal layer for wiring' 5 is embedded in the slits or openings formed in the insulating layer 2 by methods such as sputtering or CVD method, so that the thickness thereof is greater than the depth of the slits or openings formed in the insulating layer 2. As for the metal layer 5, a tungsten layer, an aluminum layer or a copper layer is generally used.

Next, as shown in FIG. 2 (E), surplus components of the metal layer 3, 5 and the adhesion layer 4 other than the components among the slits and openings are removed by polishing.

For polishing the metal layers 3, 5 and the adhesion layer 4, an abrasive composition, which comprises an abrasive particle such as aluminum oxide or silicon oxide and an oxidizing agent such as hydrogen peroxide is usually used.

When the abrasive particle for polishing the metal layers 3, 5 and the adhesion layer 4 is aluminum oxide, for example, aluminum oxide of which crystalline form is α -type has high hardness and manifests high polishing rate, but such aluminum oxide produces the disadvantages that defects such as micro scratches and orange peel effects are formed on the surface of the metal layer 5 and the insulating layer 2. Alternatively, when the abrasive particle is transition alumina such as γ -type aluminum oxide, amorphous aluminum oxide or silicon oxide, which has lower hardness than the α -type, the abrasive particle can suppress the forming of defects such as micro scratches and orange peel effects on the surface of the metal layer 5 and the insulating layer 2, but it causes the disadvantage that sufficient polishing rate can not be obtained in polishing the metal layers 3, 5 and the adhesion layer 4.

Also, it is known to use cerium oxide as an abrasive particle for the insulating layer 2. However, it is said that cerium oxide is not suitable for polishing of the metal layers 3, 5 and the adhesion layer 4 on a semiconductor substrate, since the insulating layer 2 is unnecessarily polished on the completion of polishing and planarizing of the insulating layer 2 is lost and defects such as micro scratches and orange peel effects are caused on the insulating layer 2. Further, cerium oxide of which purity is low contains a radioactive isotope as impurities, therefore, when such cerium oxide is used as an abrasive particle, there is a problem that soft error is caused by α -ray radiated from the contained radioactive isotope if it remains on the device. On the other hand, high-purity cerium oxide without such impurities is very expensive and it is difficult to industrially apply the high-purity cerium oxide as an abrasive particle because of the cost.

As described above, when polishing is conducted using the conventional polishing composition for planarizing a metal layer on a semiconductor substrate in a process for producing a semiconductor, there are problems that defects occur on the polished surface, polishing rate is slow, polishing selectivity against a metal layer and an insulating layer is low, impurities which radiate α -ray remain. On the contrary, the present invention provides an abrasive composition which can be used as a polishing composition which is inexpensive, which provides for high polishing rate without causing defects on a metal layer formed on a

Examples thereof include an alkoxide method in which an aluminum or silicon alkoxide (for example, aluminum isopropoxide, aluminum ethoxide, aluminum n-isopropoxide or aluminum n-butoxide) is hydrolyzed in alcohol, and a vapor phase method in which a compound such as an aluminum halide or silicon halide (for example, aluminum chloride, aluminum bromide, aluminum iodide, silicon chloride, silicon bromide or silicon iodide) is vaporized, and hydrolyzed by calcining in an oxygen hydrogen flame. The oxide obtained by these methods comprises secondary particles having a particle size of 2 μm or less which are generally formed by aggregation of primary particles having a mean particle size of about 0.01 μm to about 0.2 μm .

The cerium compound which is used in the present invention is not particularly restricted, and is preferably a cerium compound of which valence is III or IV and which is dissolved or uniformly dispersed in a solvent in which the oxide (i) or the precursor which is converted to the oxide (i) by calcination is suspended. Examples thereof include cerium salts such as cerium nitrate, cerium acetate, cerium sulfate, cerium chloride, cerium oxalate, cerium carbonate, cerium ammonium sulfate and cerium nitrate such as cerium ammonium nitrate. Examples of the preferable cerium salts include cerium nitrate, cerium acetate, cerium sulfate and cerium chloride.

The abrasive particles of the present invention can be produced by a method which comprises suspending the oxide (i) or the precursor in a solvent wherein the precursor is able to be converted to the oxide (i) by calcination, to prepare a suspension, mixing a cerium compound with the suspension, removing the solvent, drying the suspension and calcining it at about 600° C. to about 1100° C. for one minute or more, preferably about 10 minutes to about 5 hours. When the above-mentioned suspension is dried, the dryer used is not particularly restricted, and a flash dryer or air flow dryer is preferably used to obtain a minute dried powder which tends not to agglomerate.

When the calcining temperature is lower than about 600° C., the cerium compound is not completely converted to cerium oxide, and when over about 1100° C., the particle size becomes too large and α -alumina is formed, which can cause defects on the polished surface if used in an abrasive composition.

Further, when aluminum oxide is used as the oxide (i) in the present invention, it is preferable to conduct calcining so that the crystalline form of aluminum oxide after calcination is mainly transition alumina such as γ -alumina, amorphous alumina or a mixture thereof. To do so, it is preferable to adopt the above-mentioned calcining temperature and time as calcining conditions.

A calcining apparatus is not particularly restricted in the present invention, and there can be used known calcining furnaces such as a rotary kiln, a flash calcining furnace, a pacing-type calcining furnace, a fluidized calcining furnace, a tunnel furnace, a vacuum furnace or a shuttle furnace. In general, from the viewpoint of productivity and heat resistance of a material of the furnaces, the rotary kiln, tunnel furnace and shuttle furnace are preferred.

The observation by a transmission electron microscope of surface of the oxide (i) containing cerium oxide in the present invention obtained in the above-mentioned method reveals that the surface is in any condition selected from a condition in which the whole surface of the oxide (i) is coated with cerium oxide, a condition in which a part of the surface of the oxide (i) is coated with cerium oxide and a

condition in which cerium oxide is contained in particles of the oxide (i). The mean particle size of the oxide (i) containing cerium oxide is not more than about 2 μm , preferably from about 0.2 to about 1.5 μm .

The abrasive composition of the present invention can be used for polishing and planarizing a metal layer on a semiconductor substrate, and can be used in the form of a slurry dispersed in water.

For forming the slurry, an abrasive particle, oxidizing agent and water may be mixed simultaneously and be dispersed, and any component may be mixed successively in any order to previously prepare the slurry. That is, an abrasive particle and water, an abrasive particle and oxidizing agent, an oxidizing agent and water may respectively be mixed, and when used for polishing, remaining one component, namely the oxidizing agent, water and an abrasive particle respectively may be mixed and be dispersed to obtain a slurry to be used.

To disperse these components to obtain the slurry, for example, dispersing methods using a homogenizer, ultrasonic disperser or wet atmosphere agitation mill may be used.

The content of abrasive particles based on the slurry, namely the slurry concentration is usually about 1% to about 30% by weight.

The abrasive particles of the present invention can contain water as mentioned before.

Additives such as a dispersing agent, precipitation inhibitor or defoaming agent may optionally be added to the abrasive composition of the present invention and the resulting mixture may be used for a polishing composition.

The abrasive composition of the present invention thus prepared in the form of a slurry can be used, for example, for polishing and planarizing of a metal layer on a semiconductor substrate. In this case, the abrasive composition in the form of a slurry has pH usually of about 7 or less, preferably about 5 or less.

The metal layer on a semiconductor substrate which is an object to be polished is not particularly restricted, and examples thereof include tungsten W, aluminum Al, copper Cu, titanium Ti and alloy thereof, and known metal layers for wiring, plug and metal contact layer.

As described above in detail, according to the present invention, there is provided an abrasive composition which is excellent in polishing selectivity against a metal layer and an insulating layer, polishes a metal layer at high rate, and has low α -ray radiation dose which will be a cause of soft error, by a simple method that an oxidizing agent and abrasive particles obtained by including cerium oxide in an oxide (i) selected from aluminum oxide and silicon oxide are mixed. The composition has extremely high industrial availability as an abrasive composition for surface treatment of a magnetic disk substrate and metal as well as for polishing of a metal layer on a semiconductor substrate.

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

In Examples and Comparative Examples, the measurements were conducted according to the following methods. Mean particle size:

A particle size at 50% cumulation was measured by a Micro track MK II particle size analyzer (SPA model 7997-20 manufactured by Nikkiso Co., Ltd.), and was recognized as mean particle size. The term "mean particle size" of the present invention means mean particle size of the secondary particles measured by this method.

mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1. and the results of the measurements are shown in Table 2.

EXAMPLE 5

An aluminum oxide powder containing cerium oxide was obtained in the same manner as in Example 2 except that the calcination of the dried powder was conducted at 850° C. for 3 hours instead of 1050° C. for 3 hours in Example 2. This aluminum oxide powder had a crystalline form of amorphous material, and had a mean particle size of 2.1 μm , and a BET specific surface area of 128 m^2/g .

Using 9 g of the aluminum oxide powder containing cerium oxide thus obtained, 150 g of a polishing slurry was obtained in the same manner as in Example 1. The secondary particles after wet-grinding had a mean particle size of 0.39 μm , and a BET specific surface area of 129 m^2/g . To this polishing slurry was added 150 g of a 10% by weight aqueous solution of iron (III) nitrate 9 hydrate as an oxidizing agent, and they were mixed to obtain an abrasive composition. The mixing ratio by weight of the polishing slurry to the aqueous solution of iron (III) nitrate 9 hydrate herein was 1:1, the slurry concentration of the aluminum oxide powder containing cerium oxide was 3% by weight.

Using the resulting abrasive composition, a tungsten layer, titanium layer and silicon oxide layer were respectively polished in the same manner as in Example 1. The mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1, and the results of the measurements are shown in Table 2.

COMPARATIVE EXAMPLE 1

The same procedure as in Example 1 was conducted except that 9 g of a γ -alumina powder having a mean particle size of 0.40 μm and a BET specific surface area of 150 m^2/g was used instead of the aluminum oxide powder containing cerium oxide in Example 1, to obtain 150 g of a polishing slurry. Into this polishing slurry was mixed 150 g of a 10% by weight aqueous solution of iron (III) nitrate 9 hydrate as an oxidizing agent to obtain an abrasive composition. The mixing ratio by weight of the polishing slurry to the aqueous solution of iron (III) nitrate 9 hydrate herein was 1:1, the slurry concentration of the γ -alumina powder was 3% by weight.

Using the resulting abrasive composition, a tungsten layer, titanium layer and silicon oxide layer were respectively polished in the same manner as in Example 1. The mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1, and the results of the measurements are shown in Table 2.

COMPARATIVE EXAMPLE 2

The same procedure as in Example 1 was conducted except that 9 g of an α -alumina powder having a mean particle size of 0.39 μm and a BET specific surface area of 25 m^2/g was used instead of the aluminum oxide powder containing cerium oxide in Example 1, to obtain 150 g of a polishing slurry. Into this polishing slurry was mixed 150 g of a 10% by weight aqueous solution of iron (III) nitrate 9 hydrate as an oxidizing agent to obtain an abrasive composition. The mixing ratio by weight of the polishing slurry to the aqueous solution of iron (III) nitrate 9 hydrate herein was 1:1, the slurry concentration of the α -alumina powder was 3% by weight.

Using the resulting abrasive composition, a tungsten layer, titanium layer and silicon oxide layer were respec-

tively polished in the same manner as in Example 1. The mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1, and the results of the measurements are shown in Table 2.

COMPARATIVE EXAMPLE 3

The same procedure as in Example 1 was conducted except that a mixed powder consisting of (i) 7.2 g of a γ -alumina powder having a mean particle size of 0.40 μm and a BET specific surface area of 150 m^2/g and (ii) 1.8 g (amount corresponding to 20% by weight in terms of cerium based on γ -alumina) of a cerium oxide powder having a mean particle size of 0.3 μm and a BET specific surface area of 105.5 m^2/g was used instead of the aluminum oxide powder containing cerium oxide in Example 1, to obtain 150 g of a polishing slurry. Into this polishing slurry was mixed 150 g of a 10% by weight aqueous solution of iron (III) nitrate 9 hydrate to obtain an abrasive composition. The mixing ratio by weight of the polishing slurry to the aqueous solution of iron (III) nitrate 9 hydrate herein was 1:1, the slurry concentration of the mixed powder was 3% by weight, and the pH of the slurry was 1.1.

Using the resulting abrasive composition, a tungsten layer, titanium layer and silicon oxide layer were respectively polished in the same manner as in Example 1. The mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1, and the results of the measurements are shown in Table 2.

COMPARATIVE EXAMPLE 4

9 g of the aluminum oxide powder containing cerium oxide obtained in Example 2 was dispersed in 291 g of water to obtain a 3% by weight of slurry. This slurry was wet-ground and pH thereof was prepared to be 1.1 by adding of nitric acid to obtain a polishing slurry.

Using the resulting abrasive composition, a tungsten layer, titanium layer and silicon oxide layer were respectively polished in the same manner as in Example 1. The mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1, and the results of the measurements are shown in Table 2.

COMPARATIVE EXAMPLE 5

An aluminum oxide powder containing cerium oxide was obtained in the same manner as in Example 1 except that the amount of cerium nitrate was changed to 15.81 g (amount of corresponding to 3 parts by weight in terms of cerium based on aluminum oxide equivalent). This powder had a crystalline form of γ -alumina, and had a mean particle size of 0.9 μm , and a BET specific surface area of 55 m^2/g .

Using 9 g of the aluminum oxide powder containing cerium oxide thus obtained, 150 g of a polishing slurry was obtained in the same manner as in Example 1. To this polishing slurry was added 150 g of a 10% by weight aqueous solution of iron (III) nitrate 9 hydrate as an oxidizing agent, and they were mixed to obtain an abrasive composition. The mixing ratio by weight of the polishing slurry to the aqueous solution of iron (III) nitrate 9 hydrate herein was 1:1, the slurry concentration of the aluminum oxide powder containing cerium oxide was 3% by weight.

Using the resulting abrasive composition, a tungsten layer, titanium layer and silicon oxide layer were respectively polished in the same manner as in Example 1. The mean particle size of the abrasive particle and composition abstract of the abrasive composition are shown in Table 1, and the results of the measurements are shown in Table 2.

and the results of the measurements are shown in Table 2.

the composition polishes an insulating layer only at low

TABLE 1

	Abrasive particles	Mean particle size	Content of cerium(*)	Oxidizing agent	pH of a slurry
Example	1 aluminum oxide containing cerium oxide	0.5 μm	10 wt %	$\text{Fe}(\text{NO}_3)_3$	1.1
	2 aluminum oxide containing cerium oxide	0.5 μm	20 wt %	$\text{Fe}(\text{NO}_3)_3$	1.1
	3 aluminum oxide containing cerium oxide	0.5 μm	20 wt %	H_2O_2	3.8
	4 aluminum oxide containing cerium oxide	0.5 μm	20 wt %	H_2O_2	7
	5 amorphous aluminum oxide containing cerium oxide	0.4 μm	20 wt %	$\text{Fe}(\text{NO}_3)_3$	1.1
Comparative Example	1 γ -alumina	0.4 μm	None	$\text{Fe}(\text{NO}_3)_3$	1.1
	2 α -alumina	0.4 μm	None	$\text{Fe}(\text{NO}_3)_3$	1.1
	3 a mixture of γ -alumina and cerium oxide	0.4-0.3 μm	20 wt %	$\text{Fe}(\text{NO}_3)_3$	1.1
	4 aluminum oxide containing cerium oxide	0.5 μm	20 wt %	None	1.1
	5 aluminum oxide containing cerium oxide	0.9 μm	3 wt %	$\text{Fe}(\text{NO}_3)_3$	1.1
	6 aluminum oxide containing cerium oxide	2.5 μm	10 wt %	$\text{Fe}(\text{NO}_3)_3$	1.1
	7 cerium oxide	3.5 μm	CeO_2 only	$\text{Fe}(\text{NO}_3)_3$	1.1
	8 aluminum oxide containing cerium oxide	0.5 μm	20 wt %	H_2O_2	9
	9 γ -alumina	0.4 μm	None	H_2O_2	3.8
	10 α -alumina	0.4 μm	None	H_2O_2	3.8
	11 a mixture of γ -alumina and cerium oxide	0.5 μm	20 wt %	None	3.8
	12 amorphous aluminum oxide containing cerium oxide	0.4 μm	20 wt %	None	1.1

(*): based on aluminum oxide

TABLE 2

		Tungsten layer		Titanium layer		Silicon oxide layer	
		Polishing rate ¹⁾ ($\text{\AA}/\text{min}$)	Surface appearance ²⁾	Polishing rate ¹⁾ ($\text{\AA}/\text{min}$)	Polishing rate ³⁾ ($\text{\AA}/\text{min}$)	Surface appearance ²⁾	
Example	1	4700	Mirror surface	900	15	No defect	
	2	7500	Mirror surface	1400	10	No defect	
	3	3000	Mirror surface	1400	18	No defect	
	4	3500	Mirror surface	1000	25	No defect	
	5	7500	Mirror surface	1100	10	No defect	
Comparative Example	1	1700	Mirror surface	320	45	No defect	
	2	7500	Mirror surface	1600	40	Some scratches are observed	
	3	2000	Mirror surface	350	36	No defect	
	4	190	Mirror surface	350	40	No defect	
	5	2000	Mirror surface	670	15	No defect	
	6	4500	Mirror surface	800	18	Some scratches are observed	
	7	6000	Mirror surface	600	25	Some scratches are observed	
	8	4000	Non-mirror surface	700	80	No defect	
	9	840	Mirror surface	500	54	No defect	
	10	5500	Mirror surface	3500	81	Some scratches are observed	
	11	200	Mirror surface	360	54	No defect	
	12	180	Mirror surface	350	40	No defect	

In the tables,

- 1) The polishing rate was shown based on decrease in thickness of the polished layer by way of measurement of decrease in weight of the layer.
- 2) "Mirror surface" indicates the surface condition which can reflect an object on the metal surface like a mirror when observed by an optical microscope, and "Non-mirror surface" indicates the surface condition which can not reflect an object on the metal surface like a mirror since the metal surface is rough.
- 3) The polishing rate was shown based on decrease in thickness of the polished layer, measured by layer thickness measuring apparatus (MCPD-2000, manufactured by Otsuka Electronics Corp.)

Table 2 shows that the abrasive composition of the present invention polishes a metal layer such as a tungsten layer and a titanium layer formed on a semiconductor substrate at high polishing rate without causing defects such as micro scratch and orange peel on the surface of the metal layer, although

polishing rate. The composition also polishes the insulating layer without causing defects on the surface of the insulating layer. This indicates the composition has excellent polishing selectivity against a metal layer and an insulating layer without causing defects on the surface of both the metal layer and the insulating layer and does not unnecessarily polish the insulating layer. From the results of Example 1, it is known that the abrasive composition of the present invention has extremely low α -ray radiation dose which will be a cause of soft error.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a polishing apparatus using the CMP method. Here, letter (a) indicates a wafer, letter (b) indicates a polishing pad, letter (c) indicates a wafer carrier, letter (d) indicates a polishing platen and letter (e) indicates a polishing composition respectively.

FIG. 2 is a sectional view showing one example for forming an embedded metal wiring board using the conven-

[54] PROCESS FOR MANUFACTURE OF METAL OXIDE

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[73] Assignee: Kabushiki Kaisha Advance, Tokyo, Japan

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[22] Filed: Dec. 24, 1987

[30] Foreign Application Priority Data

Dec. 27, 1986 [JP] Japan 61-309017

[51] Int. Cl.⁴ C04B 35/00

[52] U.S. Cl. 423/339; 423/335; 423/592; 423/604; 423/608; 423/610; 423/618; 423/619; 423/622; 423/624; 423/625; 423/635; 423/636; 423/641

[58] Field of Search 423/335, 339, 592, 604, 423/608, 610, 618, 619, 622, 624, 625, 635, 636, 641

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Assistant Examiner—Wayne A. Langel

Attorney, Agent, or Firm—Finnegan, Henderson, Farabow, Garrett & Dunner

[57] ABSTRACT

An improved process for the manufacture of a metal oxide is disclosed. In the process wherein a hydrolyzable organometallic compound is hydrolyzed by an alkaline hydrolyzing agent in an alkaline organic solvent, and thereafter, the metal oxide is formed by a condensation reaction of a metal hydroxide resulting from the hydrolysis of the organometallic compound, the improvement comprises feeding the organometallic compound and the hydrolyzing agent into the organic solvent so that a concentration of the hydrolyzed compound is initially above a critical level of supersaturation, and thereafter, is maintained in a range from above an upper limit of solubility to the critical level of supersaturation. According to the above process, the metal oxide can be obtained in the form of a powder material with a uniform particle size distribution.

10 Claims, 8 Drawing Sheets

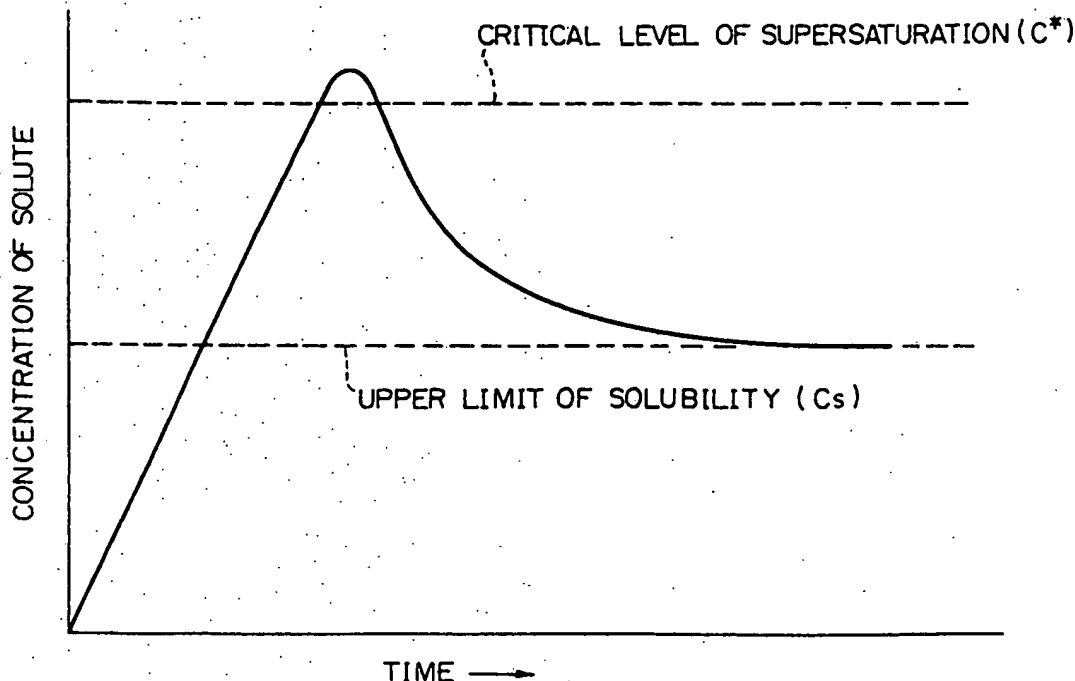


Fig. 1

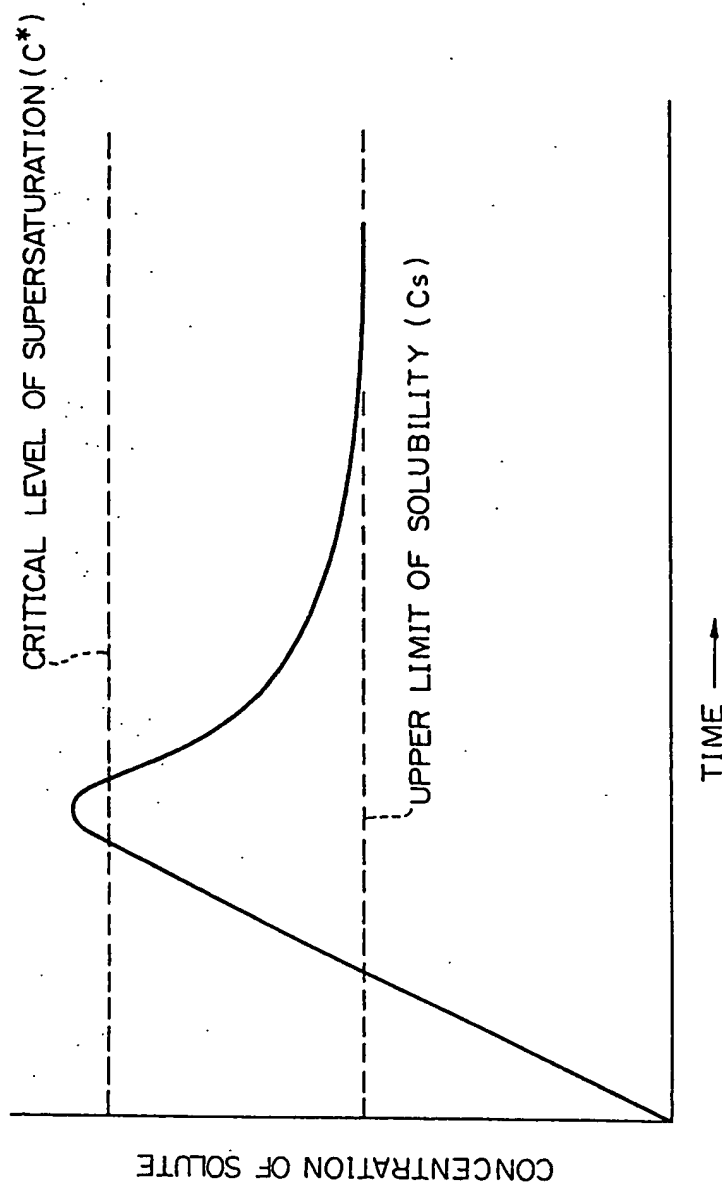


Fig. 2

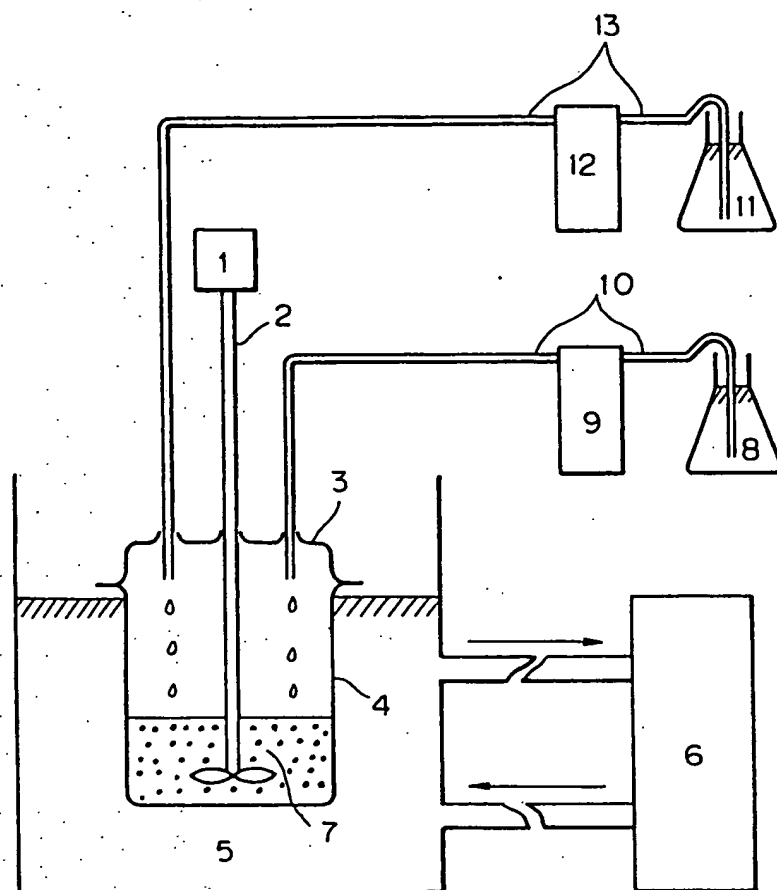


Fig. 3

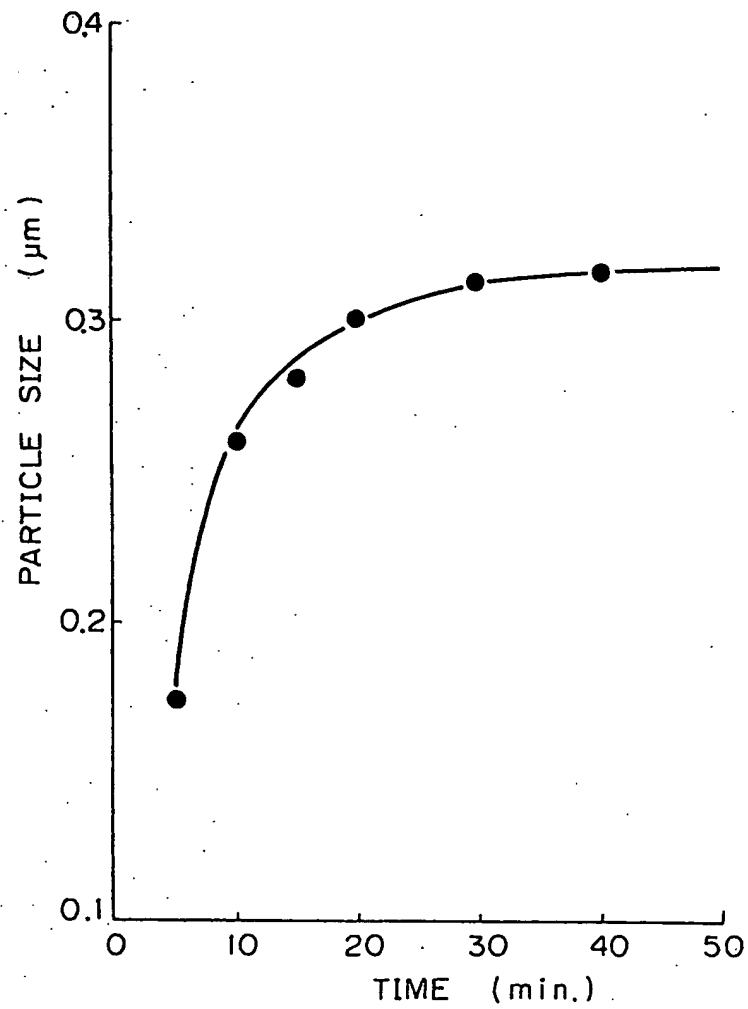


Fig. 4

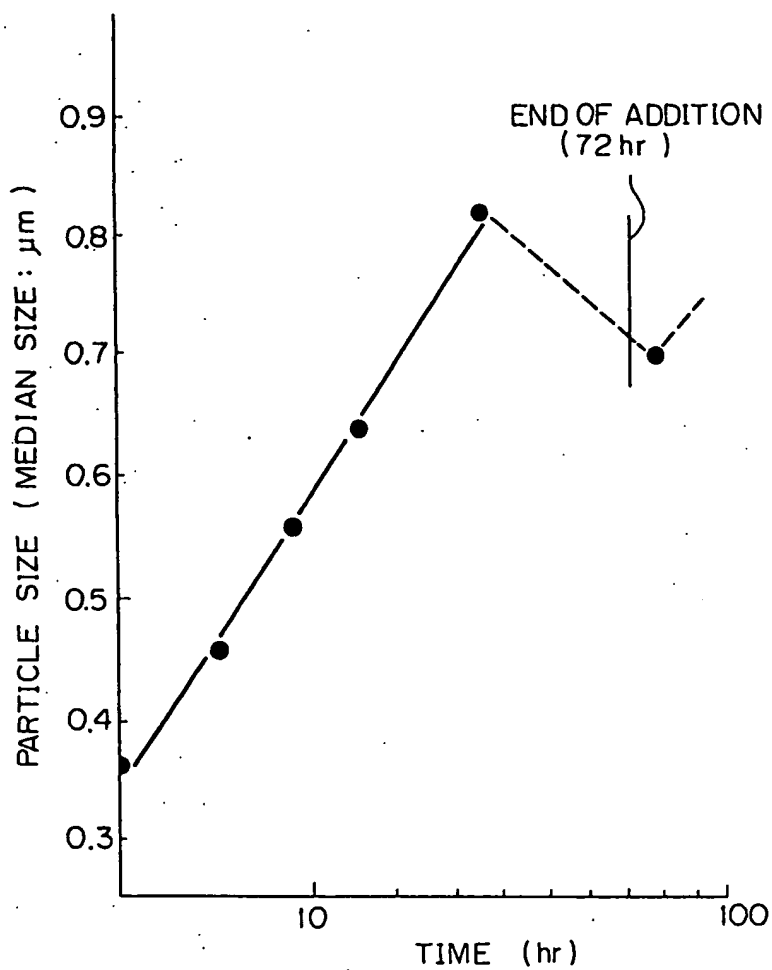


Fig. 5

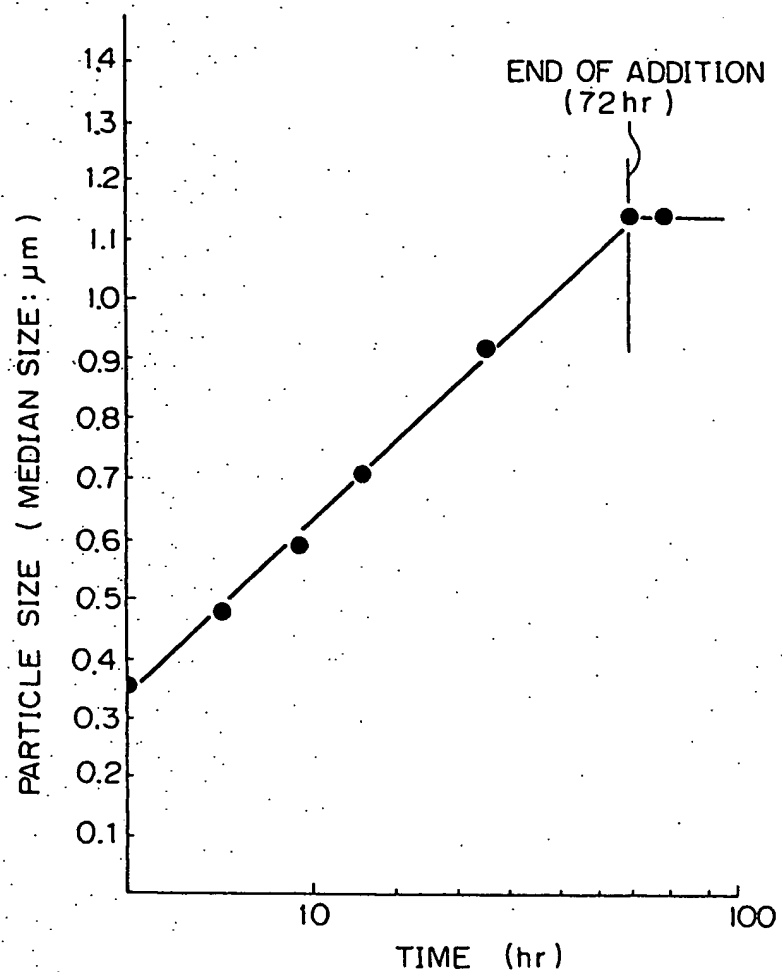


Fig. 6

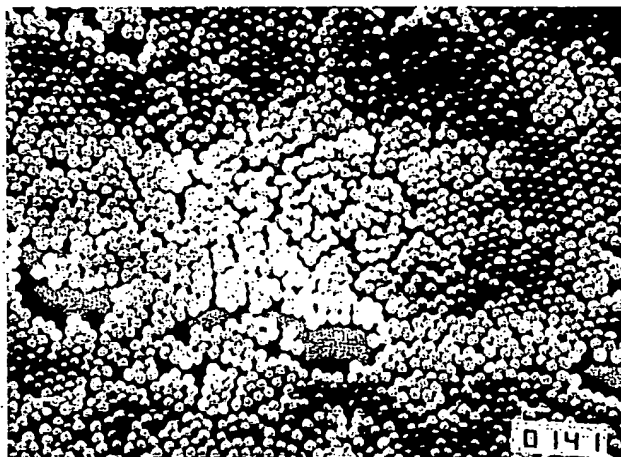


Fig. 7

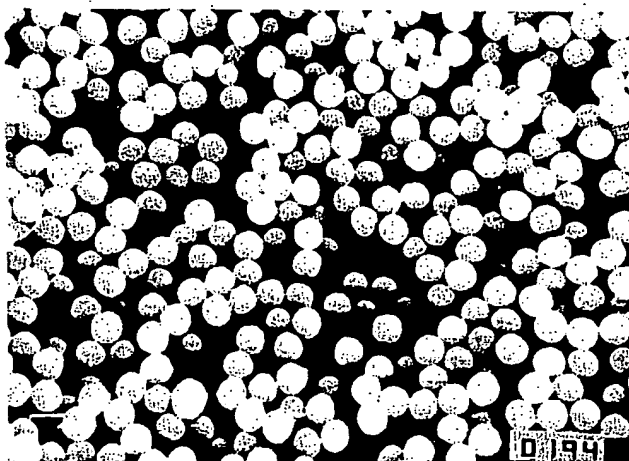


Fig. 8

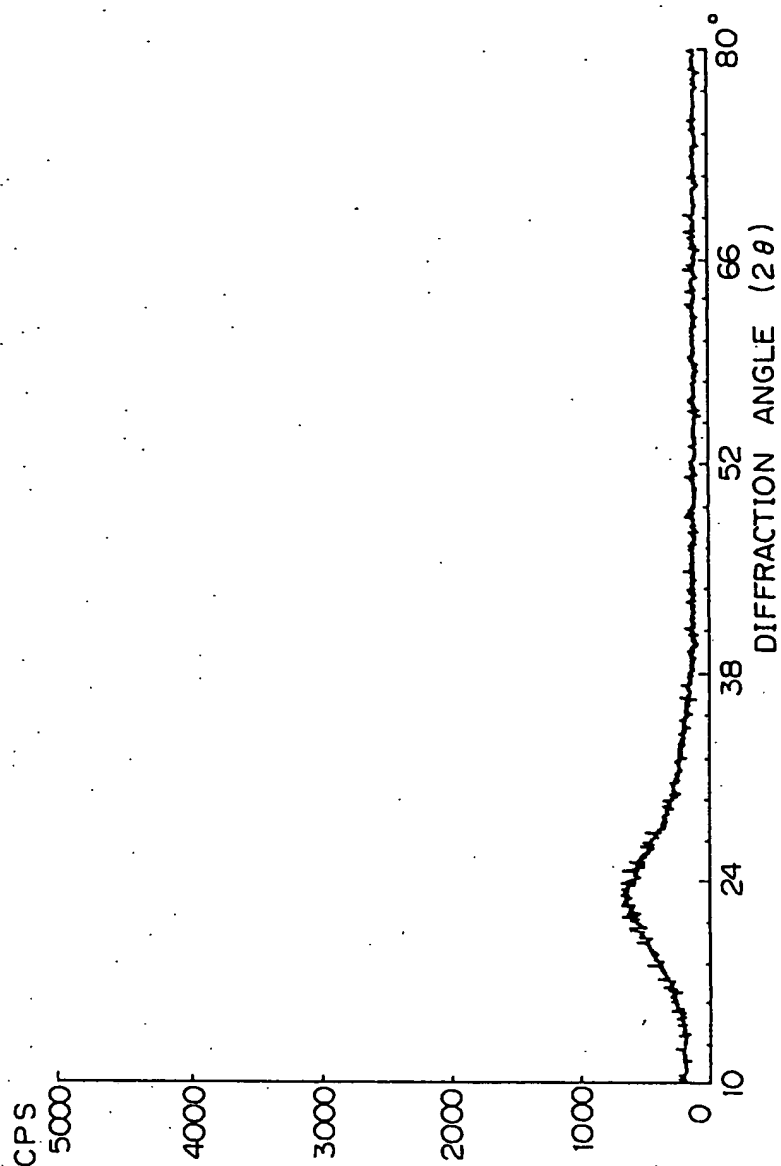
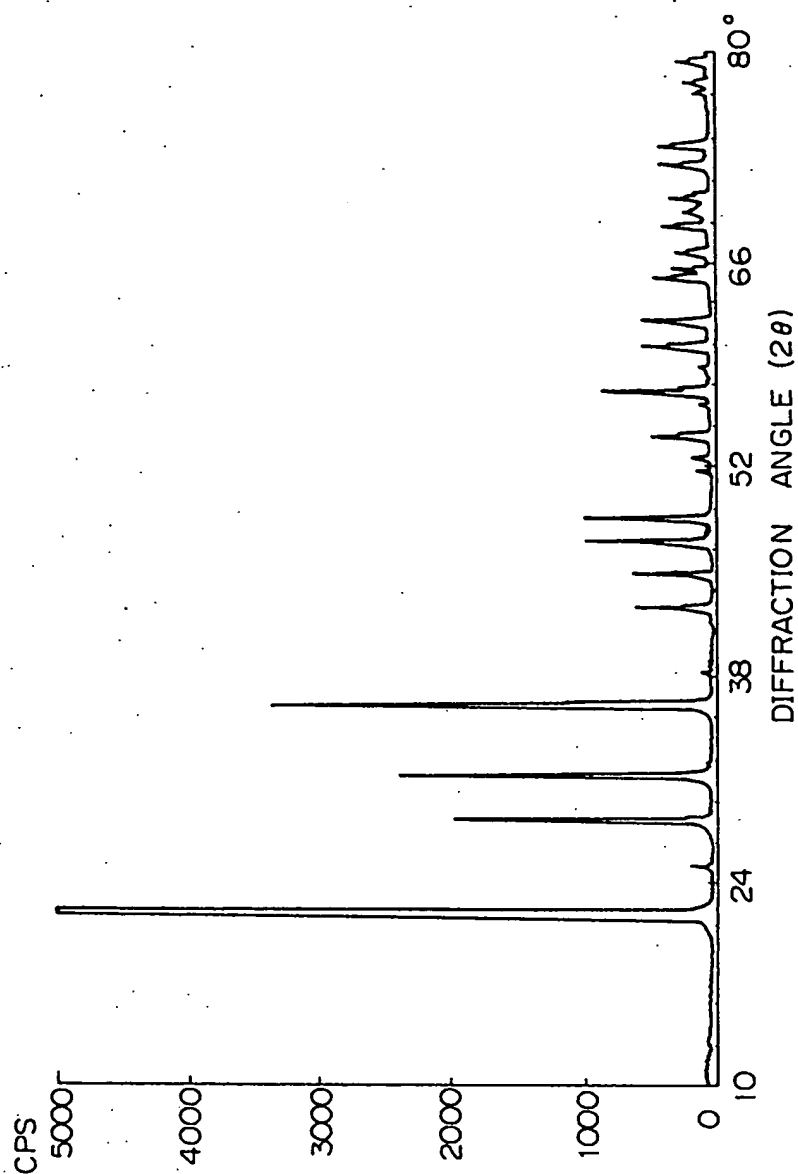


Fig. 9



PROCESS FOR MANUFACTURE OF METAL OXIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an improved process for the manufacture of a metal oxide.

2. Description of the Related Art

When a fine powder of inorganic oxide is produced by an industrial process, a bulk of the inorganic oxide is ground to fine powders more than several microns (μm) in size, and it is difficult to obtain a finer powder by a known grinding process.

Recently, it has become possible to obtain an ultrafine powder material of several hundreds of angstrom (\AA) in size by a vapor-phase reaction. However, it is difficult to apply such a method for a production of a bigger powder. There is a demand for a process for manufacturing a powder material with a uniform particle size, i.e., a narrow distribution of a particle size which ranges from 0.1 μm to several microns.

Several attempts have been made to meet such a demand. For example, Takajiro Shimohira mentioned in the Report of the National Institute for Research in Inorganic Materials, Science and Technology Agency, No. 14, pages 49-58, 1977; that, to produce SiO_2 powder, a certain amount of ethyl silicate and a certain amount of an aqueous ammonia are reacted batchwise to grow the powder to about 0.3 μm while realizing a narrow distribution of the uniform particle size.

In the above method, however, a concentration of alkoxide must be raised to increase the particle size, and this raising of the concentration can affect the uniformity of the size distribution. Therefore, a range of the concentration which is practically operable is extremely limited.

To solve this problem, an attempt was made wherein fine powder materials produced by the above process and having a narrow distribution of the particle size were introduced into a fresh reaction system, with the intention of growing the powder in a batchwise reaction by using the fine powder materials as a core. However, the growth of the powder materials was accompanied by a formation of fresh grains, and thus the size distribution was adversely affected.

In addition to SiO_2 powder, there were attempts to produce an inorganic oxide powder with a narrow distribution of size by a batchwise reaction, but a successful method of controlling the size distribution has not been found. As stated above, it is difficult to obtain a powder material having a narrow distribution of size ranging from 0.1 μm to several microns, by a batchwise reaction.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a practical process for stably manufacturing a fine powder oxide with the narrow distribution of any size, by feeding an organometallic compound and a hydrolyzing agent into a reaction medium at a given rate to control the reaction rates of the hydrolysis and condensation reaction.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a process for the manufacture of a metal oxide wherein a hydrolyzable organometallic compound is

hydrolyzed by an alkaline hydrolyzing agent in an organic solvent, and thereafter, the metal oxide is formed by a condensation reaction of a metal hydroxide resulting from the hydrolysis of the organometallic compound. This process is characterized in that the organometallic compound and the hydrolyzing agent are fed into the organic solvent so that a concentration of the hydrolyzed compound is initially above a critical level of supersaturation, and thereafter, is maintained in a range from above an upper limit of solubility up to the critical level of supersaturation.

Further, the present invention provides the metal oxide prepared by the above process.

BRIEF EXPLANATION OF THE DRAWINGS

FIG. 1 is a graph illustrating a principle of the process of the present invention;

FIG. 2 shows an apparatus for carrying out the present process;

FIG. 3 is a graph illustrating a powder growth in a conventional process;

FIG. 4 is a graph illustrating a powder growth in another conventional process;

FIG. 5 is a graph illustrating a powder growth in the process according to the present invention;

FIG. 6 is an electron micrograph of a powder material before a growth step, prepared according to the present process;

FIG. 7 is an electron micrograph of a powder material after a growth step, prepared according to the present process;

FIG. 8 is an X-ray diffraction pattern of a powder material prepared according to the present process; and

FIG. 9 is an X-ray diffraction pattern of a powder material after calcination of the material of FIG. 8.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the process of the present invention, any known organometallic compound may be employed so long as it is hydrolyzable. Preferably the compound used has a structure such that a metallic element present in the compound is bonded to an organic moiety therein via an oxygen atom.

In a preferred embodiment of the present invention, the metallic element is selected from a group consisting of the elements belonging to Groups I to IV of the Periodic Table. More particularly, the metallic element is, for example, lithium (Li), sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), potassium (K), calcium (Ca), scandium (Sc), titanium (Ti), copper (Cu), zinc (Zn), gallium (Ga), germanium (Ge), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), indium (In), tin (Sn), cesium (Cs), barium (Ba), lanthanoid (Ln), hafnium (Hf), mercury (Hg), thallium (Tl), and lead (Pb).

The more preferable metallic element is Li, K, Na, Mg, Ca, Sr, Al, Y, Ga, Sc, La, In, Ti, Zr, Si, Sn, or Ge.

The organic moiety present in the organometallic compound is, for example, alkyl or alkenyl having 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms.

The typical organometallic compound which can be used in the present invention is a metal alkoxide compound of the formula



wherein M represents the metallic element as defined above, R represents a hydrocarbon group, preferably lower alkyl or alkylene, and x is an integer of 1 to 6. Examples of the metal alkoxide compounds will be exemplified hereinafter.

Alkoxides of the metallic element of Group I are, for example, organosodium compounds, such as NaOCH_3 , NaOC_2H_5 or NaOC_3H_7 , or similar compounds wherein Li, K or the like is substituted for Na in the organosodium compounds.

Alkoxides of the metallic element of Group II are, for example, organomagnesium compounds, such as $\text{Mg}(\text{OCH}_3)_2$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, $\text{Mg}(\text{OC}_3\text{H}_7)_2$, $\text{Mg}(\text{OC}_4\text{H}_9)_2$, $\text{Mg}(\text{OC}_5\text{H}_{11})_2$ or $\text{Mg}(\text{O}_2\text{C}_2\text{H}_5)_2$ or similar compounds wherein Ca, Zn, Sr, Ba, Cd, etc., is substituted for Mg in the compounds.

Alkoxides of the metallic element of Group III are, for example, organoaluminum compounds, such as $\text{Al}(\text{OC}_2\text{H}_5)_3$, $\text{Al}(\text{OC}_3\text{H}_7)_3$ or $\text{Al}(\text{OC}_4\text{H}_9)_3$ or similar compounds wherein Ga, etc., is substituted for Al in the compounds.

Alkoxides of the metallic element of Group IV are, for example, organosilicone compounds, such as $\text{Si}(\text{OCH}_3)_4$, $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(\text{O-iso-C}_3\text{H}_7)_4$, $\text{Si}(\text{O-n-C}_3\text{H}_7)_4$, $\text{Si}(\text{O-n-C}_4)_4$, $\text{Si}(\text{OC}_5\text{H}_{11})_4$ or similar compounds wherein Ti, Zr, Ge, Sn, Hf, etc., is substituted for Si in the compounds.

The alkaline hydrolyzing agent may be any known compound capable of hydrolyzing the organometallic compound used. Examples of the alkaline hydrolyzing agent are hydroxides of alkali metals (i.e., sodium, potassium), and ammonia. In general, the hydrolyzing agent is used in the form of an aqueous solution. The kind of the hydrolyzing agent and the pH value may vary with the kind of the organometallic compound to be hydrolyzed. For example, a silicon alkoxide is conveniently hydrolyzed by an aqueous ammonia having a pH of 9.0 to 12.0.

In the process according to the present invention, it is convenient to feed each of the organometallic compound and the aqueous solution of the hydrolyzing agent in the form of a solution in an organic solvent. As such an organic solvent, it is possible to use any organic solvent which can dissolve the organometallic compound and the aqueous solution of the hydrolyzing agent. From the viewpoint of operability and availability, it is better to employ an alcohol such as methanol, ethanol, isopropanol, butanol, isoamyl alcohol, ethylene glycol, or propylene glycol.

As an organic solvent into which the organometallic compound and the aqueous hydrolyzing agent are fed, preferably in the form of the solution, any organic solvent which is inert to the reactants and products may be used. Preferably the same solvent is used as that for the above feed solution.

When practicing the process of the present invention, the organometallic compound is generally dissolved in the organic solvent to form a stock liquid A. On the other hand, the aqueous solution of the hydrolyzing agent is also dissolved in the organic solvent (which may be different from the above solvent, but is preferably the same) to form a separate stock liquid B. Further, the aqueous solution of the hydrolyzing agent is added to the separate organic solvent to form a reaction medium which is charged into a reaction vessel.

Then, the stock liquids A and B are introduced to the reaction vessel at given feeding rates. The stirring of the reaction solution is started before the introduction of

the stock liquids and continued until the reaction is completed.

The feeding rate may be constant. In order to effectively control the particle size obtained, the feeding rate can be fast in a first stage wherein a grain seed is formed, and slow in a second stage wherein a powder material is grown from the seed. The particle size obtained can be controlled by reaction conditions. For example, the lower the temperature of the reaction vessel, the larger the particle size; the higher the polarity of the solvent, the smaller the particle size.

After the particle size of the powder material reaches the desired level, the product is separated from the solvent, dried, washed, and then dried again. The resulting powder material is generally amorphous. If desired, the amorphous powder material can be calcinated, for example, for several hours at several hundreds of degrees, to obtain a crystalline material.

Further, the resulting powder material can be utilized without separation from the reaction solvent. For example, after the growth of the grain seed is completed, a binder or the like can be added to the resulting mixture, and the whole as a liquid can be applied on a substrate and then calcinated.

Although the mechanism of the process of the present invention as mentioned above is not absolutely clear, the following assumption can be made: It is believed that the present process comprises two stages, i.e., the first stage of forming a grain seed and the second stage of growing a powder material therefrom. Referring to FIG. 1, a concentration of the metal hydroxide is increased as the organometallic compound is hydrolyzed. When the concentration of the hydroxide exceeds the critical level of supersaturation (C^*), a nucleus is formed. As a result of the consumption of the solute, the concentration of the solute is lowered, and therefore, the formation of the grain seed ceases. Thereafter, the solute is consumed only for the growth of the grain seed until the concentration thereof reaches to the upper limit of solubility (C_s).

In order to produce the powder material having the uniform particle size, it is important to shorten a period of time when the concentration of the hydroxide exceeds the critical level of supersaturation. Further, in order to ensure a sufficient growth to the powder material, it is important to maintain the concentration of the hydroxide between the upper limit of solubility and the critical level of supersaturation.

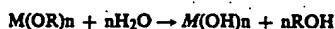
The concentration can be controlled by introducing a large amount of the organometallic compound and the hydrolyzing agent until the nuclei are formed, and then by carrying out a continuous supplement so that the concentration does not exceed the critical level of supersaturation.

The formation of the nuclei can be easily observed by transmission electron spectroscopy (TES) and scanning electron spectroscopy (SES), etc.

The supersaturation state can be easily obtained by any known technique, for example, by varying the temperature of the reaction system.

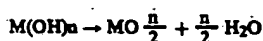
The reactions in the process according to the present invention can be schematically shown as follows:

Hydrolysis:



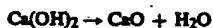
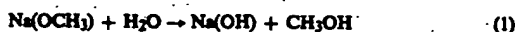
Condensation reaction:

-continued



In the above formulae, M is the metallic element; R is, for example, alkyl, and n is an integer of 1 to 4.

Typical reaction formulae are as follows:



As explained above, the product formed in accordance with the present invention is the metal oxide which comprises the metallic element as defined above and has a substantially uniform particle size. The particle size can be controlled, ranging from about 0.1 μ m to several microns. The product is generally obtained as a sphere.

The metal oxide obtained comprises predominantly amorphous material. However, a small amount of heat can bring about a crystalline product, and further, a complete amorphous product can be produced by an appropriate selection of the starting materials.

The process of the present invention brings the following advantages:

(1) By feeding the organometallic compound together with the hydrolyzing agent therefor, the particle can be grown to several microns, while realizing the narrow distribution of the particle size.

(2) Because the feeding rate of each of the organometallic compound and the hydrolyzing agent can be adjusted independently of the other, the condition of the reaction solvent in the reaction vessel can be easily controlled.

(3) Apart from the initial reaction conditions, the solvent, the hydrolyzing agent and the organometallic compound which are suitable for the particle growth can be introduced, and accordingly, the production time can be shortened.

(4) The organometallic compound can be given a high level of purity by fractionating, and therefore, a high level of purity of the resulting metal oxide can be easily obtained.

As described above, the characteristic features of the metal oxide prepared in accordance with the present invention reside in the spherical shape and the uniform particle size. Therefore, the metal oxide prepared by the present process has a superior calcination property over the convention powder metal oxide, and accordingly, the metal oxide prepared by the present process will greatly contribute to an improvement of the properties of fillers of synthetic resins, electronic materials, spacer materials, dental materials, engineering materials, or the like.

EXAMPLES

The present invention now will be further illustrated by, but is by no means limited to, the following Examples.

In the following Examples, analyses of the properties were carried out as follows, unless otherwise indicated:

Evaluation of Properties

Evaluation of the properties was mainly carried out on the basis of observation by electron micrographies, as well as measurement by a centrifugal particle size analyzer. More particularly, a shape, a particle size and a microstructure were observed by a transmission electron microscope, JEM-T20 (Nippon Denshi K.K.), and a particle size distribution was measured by a centrifugal particle size analyzer, SA-CP3 (Shimadzu Corporation).

EXAMPLE 1

This example was obtained for comparison purposes, and does not illustrate the embodiment of the present invention.

(1) Batchwise Process

In this example (1-1), commercially available reagents were used; i.e., ethanol (99.5%; guaranteed grade), aqueous ammonia (>28%; guaranteed grade), and ethyl silicate (>96%).

A reaction medium was prepared by diluting 0.1 mole of water and 0.35 mole of aqueous ammonia with ethanol to 100 ml. The reaction medium was maintained at 20° C. \pm 0.5° C. and agitated with a magnetic stirrer.

After the temperature reached the above pre-determined point, 0.035 mole of ethyl silicate was added, and after this addition, the relationship between the particle size and the elapsed time was observed. The result is shown in FIG. 3. It is apparent that the particle size reached almost the upper limit around 20 minutes after the addition.

(2) Process without Alkali

The reagents used in the above batchwise process (1) were also employed in this example (1-2). Further, the apparatus as shown in FIG. 2 was used.

A solution (50 ml) of ammonia (6.8 mole/l) and water (32 mole/l) in ethanol was prepared and charged as a reaction medium 7 into a separable flask 4 provided with a separable cover 3 and a rotating blade 2 connected to a stirring motor 1. The reaction medium 7 was maintained at 10° C. \pm 0.2° C. by circulating water 5 through a temperature controller 6.

A solution of ethyl silicate (0.4 mole/l) in ethanol was prepared and charged into a vessel 8. An amount of 50 ml of the solution was introduced into the separable flask 7, via a tube 10 by a pump 9, while maintaining the temperature at 10° C. \pm 0.2° C. The reaction mixture was then stirred for 1 hour to form nuclei.

Further, ethanol was charged in a vessel 11, and 450 ml of ethanol was then introduced into the separable flask 7 via a tube 13 by a pump 12, at a rate of 0.1 ml/min. At the same time, 450 ml of the ethanol solution of ethyl silicate was introduced from the vessel 8 to the flask 7 at the same feeding rate, to grow the nuclei. The particle size was measured as time elapsed, and the maximum size (0.82 μ m) was observed 36 hours later. Thereafter, the particle size was reduced. The size at 72 hours was 0.70 μ m. Thereafter, the reaction mixture became a paste and the spherical powder materials disappeared. The result is shown in FIG. 4.

EXAMPLE 2

This example illustrates one embodiment of the present invention.

In this example, the apparatus as shown in FIG. 2 also was used. In order to form a nucleus, a solution A₁ of ethyl silicate (0.2 mole/l) in ethanol was prepared and charged in a storage vessel (not shown). Further, a solution B₁ of ammonia (3.4 mole/l) and distilled water (16 mole/l) in ethanol was prepared and charged in a separate storage vessel (not shown). To the separable flask 7, 50 ml of the solution A₁ was introduced and maintained at 10° C. with stirring. Thereafter, 50 ml of the solution B₁ was rapidly added thereto to form the nuclei. The nuclei formed 100 minutes after said addition were observed by the transmission electron microscope (×5,000). The electron micrograph thereof is shown in FIG. 6. The particle size of the nucleus was about 0.4 μm.

A solution A₂ of ethyl silicate (0.4 mole/l) in ethanol, and a solution B₂ of ammonia (3.4 mole/l) and distilled water (8 mole/l) in ethanol were prepared and charged in the vessels 8 and 11, respectively. The solutions A₂ and B₂ were introduced at the rate of 0.75 mole/min into the flask 7 containing the nuclei. The growth of the seeds was observed and the result is shown in FIG. 5. After the addition was completed (72 hours), the electron micrograph (×5,000) of the powder material formed was taken. The result is shown in FIG. 7. The particle size was about 1.5 μm.

The powder material was dried and analyzed by an X-ray diffraction to determine the crystalline structure. The pattern is shown in FIG. 8, from which it is apparent that the powder material was amorphous. The powder material was calcinated for 1 hour at 1,500° C. and analyzed by an X-ray diffraction. The result is shown in FIG. 9, which indicates a cristobalite crystalline phase.

EXAMPLE 3

As in Example 2, various metal oxides were produced using various metal alkoxides and organic solvents listed in the following Table 1 and the particle sizes thereof were measured.

TABLE 1

Organic solvent	Metal alkoxide	Concentration at seed formation stage (mol/l)	Concentration at growth stage (mol/l)	Metallic oxide	Particle size (μm)
Isopropanol	NaOCH ₃	1.0	2.0	Na ₂ O	1.5
Isopropanol	Ca(Oiso-C ₃ H ₇) ₂	0.2	0.4	CaO	1.3
Ethanol	Al(O-nC ₄ H ₉) ₃	0.15	0.2	Al ₂ O ₃	1.2
Ethanol	Ga(O-nC ₄ H ₉) ₄	0.2	0.4	Ga ₂ O ₃	1.1
Butanol	Ti(O-nC ₄ H ₉) ₄	0.1	0.1	TiO ₂	2.0

Although the present invention has been described with reference to specific embodiments, various changes and modifications obvious to those skilled in the art are deemed to be within the spirit, scope and concept of the invention.

We claim:

1. A process for the manufacture of a metal oxide wherein a hydrolyzable organometallic compound is hydrolyzed by an alkaline hydrolyzing agent in an organic solvent, and thereafter, the metal oxide is formed by a condensation reaction of a metal hydroxide resulting from the hydrolysis of the organometallic compound, characterized in that the organometallic compound and the hydrolyzing agent are fed into the organic solvent so that a concentration of the hydrolyzed compound is initially above a critical level of supersaturation, and thereafter, is maintained in a range from above an upper limit of solubility to the critical level of supersaturation.

2. A process according to claim 1, wherein the organometallic compound has a structure such that a metallic element present in said compound is bonded to an organic moiety therein via an oxygen atom.

3. A process according to claim 2, wherein the metallic element is selected from a group consisting of the elements belonging to Groups I to IV of the Periodic Table.

4. A process according to claim 3, wherein the metallic element is selected from a group consisting of lithium (Li), sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), potassium (K), calcium (Ca), scandium (Sc), titanium (Ti), copper (Cu), zinc (Zn), gallium (Ga), germanium (Ge), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), indium (In), tin (Sn), cesium (Cs), barium (Ba), lanthanoid (Ln), hafnium (Hf), mercury (Hg), thallium (Tl), and lead (Pb).

5. A process according to claim 2, wherein the organometallic compound is a metal alkoxide.

6. A process according to claim 1, wherein the hydrolyzing agent is fed in the form of a solution comprising an organic solvent, water and the hydrolyzing agent.

7. A process according to claim 1, wherein the hydrolyzing agent is an ammonia or a hydroxide of an alkali metal.

8. A process according to claim 1, wherein the organic solvent into which the organometallic compound and the hydrolyzing agent are fed is alkaline.

9. A process according to claim 1, wherein the metal

oxide is formed in the form of a powder material with a uniform particle size distribution.

10. A process according to claim 8, wherein the powder material of the metal oxide has an average particle size of 0.1 μm to 10 μm.

* * * * *

United States Patent [19]

Shimo

[11] Patent Number: 5,064,517

[45] Date of Patent: Nov. 12, 1991

[54] METHOD FOR THE PREPARATION OF
FINE PARTICULATE-METAL-CONTAINING
COMPOUND

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[73] Assignee: Idemitsu Kosan Company Limited,
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[21] Appl. No.: 463,392

[22] Filed: Jan. 11, 1990

[30] Foreign Application Priority Data

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Jun. 14, 1989 [JP]	Japan	1-149706

[51] Int. Cl.³ C01D 1/02; B05D 3/06

[52] U.S. Cl. 204/157.51; 204/157.5;
204/157.41; 204/157.4; 427/53.1

[58] Field of Search 204/157.4, 157.41, 157.48,
204/157.5, 157.51; 427/53.1

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Primary Examiner—John F. Niebling
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Attorney, Agent, or Firm—Wyatt, Gerber, Burke and
Badie

[57] ABSTRACT

A finely divided metal-containing compound can be efficiently prepared by irradiating a mixed vapor phase of an organometallic compound in a concentration to exceed a specified lower limit and a reactant gaseous compound with laser beams having an incident energy density to exceed a specified lower limit. When the reactant gaseous compound in the vapor phase is an oxygen-containing compound, e.g., air, the resultant powdery product is an oxide of the metallic element of the organometallic compound. When the reactant gaseous compound in the vapor phase is a halogen-containing compound, e.g., methyl halides, the resultant powdery product is a halide of the metallic element of the organometallic compound. When the reactant gaseous compound is a second organometallic compound, of which the metallic element is not the same as the metallic element in the first organometallic compound, the resultant powdery product is a composite metallic powder of which the distribution of the two metallic elements is uniform throughout each particle. No particles of either one of the metallic elements alone are contained in the powder as evidenced by the EPMA analysis.

3 Claims, No Drawings

Good Process

METHOD FOR THE PREPARATION OF FINE PARTICULATE-METAL-CONTAINING COMPOUND

BACKGROUND OF THE INVENTION

The present invention relates to a method for the preparation of a metal compound in a fine particulate form or, more particularly, to a method for the preparation of a metal compound such as a halide, oxide and composite metal compound, i.e. compounds of at least two kinds of metallic elements, in a fine particulate form.

Fine powders of a metal oxide, for example, are widely used as a base material for the preparation of various kinds of ceramic-based electronic components by utilizing their unique properties. Several methods are known in the prior art for the preparation of a fine metal oxide powder, of which a typical method is the production of particles of a metal oxide in a vapor phase such as the so-called CVD method. A problem in the conventional vapor-phase methods is that the density of the metallic atoms in the vapor phase cannot be high enough so that the efficiency of the method also cannot be high. In addition, the vapor-phase reaction requires a large amount of energy in the form of, for example, light, plasma, electron beams, heat and the like resulting in high costs for the production with a problem in energy saving.

A method is known to prepare fine metal particles by the pyrolytic decomposition of a metal compound in the vapor phase. For example, Japanese patent Kokai 60-51539 teaches a method for depositing fine metal particles from the vapor phase. Chemistry and Industry, volume 15, page 247 (1985) teaches a method in which an organometallic compound in the vapor phase is decomposed by means of laser beam irradiation.

These prior art methods by the decomposition of a metal compound in the vapor phase are disadvantageous economically and in respect of the product quality since, when the energy for the decomposition is given by a laser beam, at least one photon is required to effect the decomposition reaction to produce a molecule of the metal particle so that the costs for the energy are very great in view of the expensiveness of the laser beam per unit energy even by setting aside the problems in the difficulty encountered in the control of the reaction and formation of a relatively large amount of by-products.

Fine particles of a metal halide can be prepared by bringing a purified metal into contact with a halogen gas at an elevated temperature so that the metal directly reacts with the halogen to produce a metal halide in a fine particulate form. This method is also economically disadvantageous because of the large consumption of the thermal energy.

SUMMARY OF THE INVENTION

The present invention accordingly has an object to provide a novel and improved method for the preparation of a metal-containing compound in a fine particulate form or, in particular, for the preparation of a metal oxide, a metal halide or a composite metal compound in a fine particulate form by overcoming the above described problems and disadvantages in the prior art methods.

Thus, the method of the present invention for the preparation of a metal containing compound in a fine particulate form comprises the steps of:

(a) admixing a vapor of an exothermically decomposable organometallic compound having a density of the molecules of the compound of at least 10^{15} molecules per ml in the vapor phase with a reactant compound capable of reacting with the organometallic compound to form a mixture in the vapor phase; and

(b) irradiating at least a part of the vapor phase with energy rays having an energy density of at least 10^{-4} joule per cm^2 so as to produce activated species of the organometallic compound which start an exothermic chain reaction of the organometallic compound with the reactant compound to form fine particles of the metal-containing compound.

In particular, the reactant compound is an oxygen-containing compound, a halogen containing compound or a metal-containing compound, of which the metallic element is not the same kind as that in the organometallic compound, when the desired metal-containing compound in a fine particulate form as the product of the inventive method is a metal oxide, metal halide or composite metal compound, respectively.

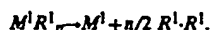
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventor has previously proposed an efficient method for the preparation of fine particles of a metal by irradiating a vapor phase of a metal-containing compound in a concentration to exceed a certain lower limit with energy rays having an energy density to exceed a certain energy density per unit area (see Japanese Patent Kokai 63-114909 and 64-11916).

The inventor has further continued investigations to develop an efficient method for the preparation of several kinds of metal containing compounds in a fine particulate form starting from a vaporizable metal compound and arrived at a discovery that the object can be achieved when an organometallic compound in the vapor phase is admixed with a vapor of a suitable reactant compound and the gaseous mixture is irradiated with energy rays provided that the organometallic compound is exothermically decomposable, the density thereof in the vapor phase exceeds a certain lower limit and the energy density of the energy rays per unit area exceeds a certain lower limit, the reactant compound being selected depending on the type of the desired metal-containing compound, so that a chain reaction is started at the irradiated site in the vapor phase to be propagated throughout the whole volume of the vapor phase forming the desired metal-containing compound in a high yield.

One of the starting materials in the inventive method is an organometallic compound which is not particularly limitative provided that the compound is vaporizable to form a vapor phase of a concentration higher than the specified lower limit and that the compound is exothermically decomposable. Preferably, the organometallic compound is an alkylated metal compound such as tetraalkyl leads, trialkyl bismuths, trialkyl thalliums, dialkyl zincs, dialkyl mercuries, dialkyl cadmiums and the like though not particularly limitative thereto. The alkyl group in the above mentioned alkylated metal compounds can be straightly linear or branched and is preferably selected from the class consisting of methyl, ethyl, n propyl and isopropyl groups.

It is essential that the organometallic compound used in the inventive method should be exothermically decomposable to produce an atom of the metal in the elementary form. Namely, the organometallic compound, which is expressed by the general formula of $M^1R^1_n$, where M^1 is an atom of a n -valent metal, R^1 is an alkyl group and n is a positive integer of, usually, 1 to 4, should be decomposed according to the following equation:



Assuming that the dissociation energy of the starting compound in the first partial reaction



is given by D_A and the recombination energy of the free radicals $R^1 \cdot$ in the second partial reaction



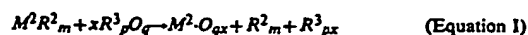
is given by D_B , then $\Delta H = D_A - D_B$. An exothermic reaction means that the value of this ΔH is negative. The reaction of the inventive method can proceed in a chain-like decomposition reaction by using an organometallic compound to meet this thermochemical requirement. It is preferable that the vapor pressure of the organometallic compound is as high as possible in order to give a high concentration of the compound in the vapor phase which ensures smooth initiation and propagation of the chain-like decomposition reaction thereof. For example, the alkyl groups in the alkylated metal compound should be a lower one, e.g., a methyl group, in this regard. It is also preferable that the absolute value of the ΔH should be as large as possible. Examples of the organometallic compound having a relatively large absolute value of ΔH include tetramethyl lead having a ΔH of -25 kcal/mole and trimethyl bismuth having a ΔH of -30 kcal/mole.

The reactant compound to be admixed with the organometallic compound in the vapor phase is selected naturally depending on the type of the desired metal-containing compound as the product. When the desired metal-containing compound to be obtained in a fine particulate form is an oxide of metal, for example, the reactant compound is a non-metal oxygen-containing compound without particular limitations provided that the compound can be in the form of a gas or vapor miscible with the vapor of the organometallic compound. The oxygen-containing compound should desirably have a relatively high vapor pressure and be readily decomposable. Examples of suitable oxygen source compounds include molecular oxygen or air and oxygen-containing gaseous compound such as nitrous oxide N_2O , nitrogen monoxide NO , nitrogen dioxide NO_2 , sulfur dioxide SO_2 and the like in respect of the relatively high vapor pressure and high reactivity with the metallic element in the atomic form produced from the organometallic compound. In particular, air is preferred as the oxygen source in respect of the easiness and safety in handling and low costs. These oxygen-containing gaseous compounds can be used either singly or as a mixture of two kinds or more according to need.

When the mixture in the vapor phase of the above described organometallic compound and the oxygen-containing compound is irradiated, at least at a part of the vapor phase, with energy rays, such as laser beams, under the conditions described later, an exothermic

chain reaction is initiated and propagated throughout the whole volume of the vapor phase to produce a metal oxide in a fine particulate form. The chain reaction proceeds by a mechanism involving partial reactions of a decomposition reaction and an oxidation reaction. The exothermic reaction here implied means a reaction in which the overall heat balance by the reaction is negative.

Assuming that the organometallic compound is an alkylated metal compound of the formula $M^2R^2_m$, in which M^2 is an atom of the metal, R^2 is an alkyl group and m is a positive rational number and the vapor of the organometallic compound is mixed with a vapor of an oxygen-containing compound of the formula $R^3_pO_q$, in which R^3 is an atom of, e.g., nitrogen or sulfur, p is zero or a positive rational number and q is a positive rational number, in a molar proportion of 1:x, x being a positive rational number, then the overall reaction is expressed by the reaction equation:



or



R^2_m in the above given Equation I is the most stable alkane compound formed by the recombination reaction of m radicals $R^2 \cdot$ formed by the decomposition reaction and R^3_{px} is the most stable compound formed from px atoms of R^3 or px molecules of R^3 formed from x moles of the oxygen-containing compound $R^3_pO_q$. $R^2_m R^3_{px}$ is the most stable compound formed by the reaction of m radicals of $R^2 \cdot$ and px atoms of R^3 or px molecules of R^3 .

When $D_A + D_B - D_C - D_D < 0$ in this reaction, assuming that D_A is the dissociation energy of the reaction $M^2R^2_m \rightarrow M^2 + mR^2 \cdot$, D_B is the dissociation energy of the reaction $R^3_pO_q \rightarrow pR^3 + q/2 O_2$ multiplied by a factor x , D_C is the recombination energy of the reaction $M^2 + x(q/2) O_2 \rightarrow M^2 \cdot O_{qx}$ and D_D is the sum of the recombination energy of the reaction $mR^2 \cdot \rightarrow R^2_m$ as the most stable alkane compound and the recombination energy of the reaction $pxR^3 \cdot \rightarrow R^3_{px}$ (in Equation I) or the recombination energy of the reaction $mR^2 \cdot + pxR^3 \cdot \rightarrow R^2_m R^3_{px}$ (in Equation Ia), then an exothermic reaction takes place to generate heat of reaction, by which a chain reaction proceeds to form the metal oxide $M^2 \cdot O_{qx}$.

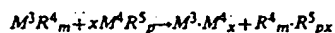
When the desired metal-containing compound in a fine particulate form as the product is a halogen compound of the metal, the reactant compound to be reacted with the organometallic compound according to the inventive method is a non-metal halogen-containing compound which is not particularly limitative provided that the compound contains at least one atom of a halogen, i.e. fluorine chlorine bromine and iodine, in a molecule and is capable of being in a gaseous form. It is preferable that the vapor pressure of the compound is as high as possible and the compound is readily decomposable. Examples of suitable halogen-containing compounds include methyl fluoride, methyl chloride, methyl bromide and methyl iodide as well as molecular halogens such as fluorine F_2 , chlorine Cl_2 , bromine Br_2 and iodine I_2 . These halogen-containing compounds can be used either singly or as a combination of two kinds or more according to need. Similar discussions can be held on the mechanism of the reaction of the

organometallic compound and the halogen-containing compound to form a metal halide to the discussions given for the reaction to form a metal oxide.

When the desired product is a composite metal compound, i.e. a compound of two kinds or more of metallic elements, in a fine particulate form, the reactant to be reacted with the organometallic compound is a metal-containing compound of which the metallic element is different from that in the organometallic compound. The reactant metal-containing compound is not particularly limitative provided that the compound can be in a gaseous form. Examples of suitable reactant metal-containing compounds include organometallic compounds having a metal-to carbon linkage, hydrides, alkoxides, carbonyls, metallocene compounds, halides, hydroxides, oxides, carbides, nitrides, sulfides and the like of a metallic or metalloid element, such as lead, bismuth, thallium, zinc, aluminum, cadmium, mercury, gold, silver, platinum, cobalt, nickel, iron, tin, silicon, germanium and the like. These metal or metalloid compounds can be used either singly or as a combination of two kinds or more according to need.

It is preferable that the reactant metal-containing compound is exothermically decomposable with a relatively small dissociation energy and that the compound has a relatively high vapor pressure in this regard, preferable reactant metal-containing compounds include the above mentioned organometallic compounds, e.g., tetramethyl lead, trimethyl bismuth, trimethyl thallium and the like, and metal halides in respect of their relatively high vapor pressure. Metal carbonyl compounds, e.g., iron carbonyl, nickel carbonyl, chromium carbonyl, molybdenum carbonyl, tungsten carbonyl and the like, are also preferable in respect of their relatively small dissociation energy to permit decomposition of the compound into the metal in an atomic state. Needless to say, the metallic element of these reactant metal-containing compounds is of a different kind from that in the organometallic compound to be reacted with these reactants. Similar discussions can be held on the mechanism of the reaction of the organometallic compound and the above defined reactant metal-containing compound to form a composite metal compound to the discussions given for the reaction to form a metal oxide.

Following is a particular discussion on the mechanism of the reaction Assume that a reaction equation



is held for the reaction taking place in a vapor phase of a mixture of an organometallic compound of the formula $M^3R^4_m$, in which M^3 is an atom of a first metallic element, R^4 is an alkyl group and m is a positive rational number, and a metal-containing reactant compound of the formula $M^4R^5_p$, in which M^4 is an atom of a second metallic element different from M^3 , R^5 is a non limitative radical to form the metal-containing compound or preferably an alkyl group, halogen atom or carbonyl group, and p is zero or a positive rational number, in a molar proportion of 1:x, x being a positive rational number. When $D_E + D_F - D_G - D_H$ in this reaction is negative, then an exothermic reaction takes place in the vapor phase resulting in proceeding of a chain reaction by the heat of reaction to produce a composite metal compound of the formula $M^3 \cdot M^4_x$. The above given D_E , D_F , D_G and D_H are defined as: D_E is the dissociation energy of $M^3R^4_m$ into $M^3 + mR^4$; D_F is the dissociation energy of $M^4R^5_p$ into $M^4 + pR^5$ multiplied by a factor x ; D_G is the recombination energy of M^3 and xM^4

into $M^3 \cdot M^4_x$; and D_H is the overall recombination energy of mR^4 and pR^5 into $R^4_m \cdot R^5_p$.

When a mixture of vapors of the organometallic compound and the reactant compound is irradiated with energy rays according to the inventive method, the concentration of the vapor of the organometallic compound in the vapor phase should be selected in consideration of the absorption coefficient of the energy rays by the vapor mixture. For example, the chain-like decomposition reaction can be initiated even with a relatively low concentration of the vapor when the absorption coefficient is increased by adequately selecting the frequency of the energy rays for irradiation. At any rate, the concentration of the organometallic compound in the vapor phase should be at least 10^{15} molecules per cm^3 or, preferably, at least 10^{16} molecules per cm^3 or, more preferably, at least 10^{17} molecules per cm^3 . When the concentration is too low, the concentration of the active species produced by the energy ray irradiation is also too low to initiate the chain reaction because the active species are deactivated to an ineffective concentration level before a reaction takes place between the active species and the reactant compound.

The concentration of the reactant compound in the vapor phase naturally depends largely on the type of the reactant compound. When the desired product is a metal oxide for example, the concentration of the reactant oxygen-containing compound in the vapor phase should be at least equimolar to the organometallic compound as calculated for the oxygen molecules O_2 . When the desired product is a metal halide, the concentration of the reactant halogen-containing compound in the vapor phase should be at least four times by moles relative to the organometallic compound as calculated for the halogen atoms.

The vapor mixture of the organometallic compound and the reactant compound can be diluted, if desired, by adding a suitable diluent gas inert to the reaction such as nitrogen, hydrogen, argon, helium and the like with an object to control the particle size distribution of the product. The degree of dilution, however, should not be too high in order to have the chain reaction proceeding smoothly. When the desired product is a composite metal compound, for example, the concentration of the diluent gas is preferably not higher than five times by moles relative to the total concentration of the organometallic compound and the reactant metal-containing compound.

The type of the energy rays to irradiate the vapor mixture is not particularly limitative provided that active species of the organometallic compound can be produced in a high concentration by the irradiation. Examples of suitable energy rays include electromagnetic waves exemplified by coherent light emitted from lasers, non-coherent light emitted from mercury lamps, xenon lamps and the like, orbital radiations, microwaves and X-rays and particle beams exemplified by ion beams, electron beams and plasma, of which laser beams, orbital radiations and X-rays are preferable or, laser beams are more preferable.

The laser beams should preferably be emitted from a high-output pulse laser. Particular examples of suitable lasers include excimer lasers and nitrogen lasers oscillating in the ultraviolet region, carbon dioxide gas lasers, carbon monoxide lasers, YAG lasers, glass lasers, ruby lasers and alexandrite lasers oscillating in the infrared region and YAG lasers oscillating in the visible region

to emit harmonics, copper-vapor lasers, gold-vapor lasers, dye lasers, argon ion lasers, krypton ion lasers and the like.

Organometallic compounds in general have high absorptivity of light in the ultraviolet region so that the active species thereof can be produced easily in a high concentration in the vapor phase by using a laser oscillating in the ultraviolet region among those named above. Excimer lasers are particularly preferable in this regard along with the relatively high energy density. Carbon dioxide gas lasers are also preferable because of the multiphoton excitation of the vibrational level possessed by the organometallic compound in the infrared region leading to decomposition of the compound. It is of course that the chain-like decomposition reaction can take place even by using a laser of other types emitting a laser beam of a wavelength at which the organometallic compound has no excitation level because the phenomenon of break-down can take place in general by the irradiation with laser beams. Although the energy rays used in the inventive method can be a continuous emission, it is preferable to use a pulse-wise emission of the energy rays in respect of the higher density of the active species easily obtained by the irradiation therewith. The energy density of the energy rays incident on the vapor phase in the inventive method should be as high as possible in order to increase the efficiency of the method.

It is an advantageous condition that the width of a single pulse of the pulse-wise irradiation in the inventive method be as small as possible so as to produce the active species in a unit time in a concentration as high as possible. In this regard, the width of a single pulse should not exceed 10^{-3} second or, preferably, should not exceed 10^{-4} second or, more preferably, should not exceed 10^{-6} second. The concentration of the activated species can not always be increased even by increasing the length of the irradiation time by a single pulse because of the increase in the probability of deactivation of the active species.

The energy density of the energy rays for irradiation should be at least 10^{-4} joule per cm^2 or, preferably, at least 10^{-3} joule per cm^2 of the cross section. When the energy density is too low, the chain reaction for the decomposition of the organometallic compound can hardly be started.

It is desirable that the irradiation with energy rays should be performed under such conditions that the organometallic compound under irradiation may have a large absorption coefficient of the radiation energy or a large extinction coefficient of light when the energy source is a laser. When tetramethyl lead is used as the organometallic compound, for example, quite satisfactory results can be obtained by using an ArF excimer laser emitting a beam at a wavelength of 193 nm since the maximum in the extinction coefficient of the compound is at a wavelength of about 200 nm.

When the vapor mixture of the organometallic compound and the reactant compound is irradiated on at least a part under the above described conditions, active species are produced in the irradiated site of the vapor phase in a concentration of $10^{15}/\text{cm}^3$ or higher or, under preferable conditions, $10^{16}/\text{cm}^3$ or higher, which initiate the exothermic chain reaction propagating to the whole volume of the vapor phase so that the reaction to form the desired metal-containing compound is almost instantaneously completed through the decomposition

of the reactants followed by the recombination reaction of the dissociated species.

It is also a possible way to obtain a metal oxide or metal halide which is a composite metal oxide or composite metal halide containing two kinds or more of metallic elements when the vapor mixture irradiated with the energy rays contains an additional metal compound capable of giving a vapor and capable of being exothermically decomposed, of which the metallic element is different from that in the organometallic compound. Such an auxiliary metal-containing compound can be the same one as in the preparation of a composite metal compound. The thus obtained composite metal oxide or composite metal halide is not a mere blend of the respective metal oxide powders or metal halide powders but a submicroscopically intimate mixture of the components.

The product of the inventive method is obtained usually in a fine particulate form of which the particle diameter rarely exceeds $1.0 \mu\text{m}$ or is mostly smaller than $0.3 \mu\text{m}$ when the product is the metal oxide or metal halide and rarely exceed $5 \mu\text{m}$ and is mostly smaller than $0.5 \mu\text{m}$ when the product is the composite metal compound.

In the following, examples are given to illustrate the inventive method in more detail but not to limit the scope of the invention in any way.

EXAMPLE 1

Vapor of tetramethyl lead was introduced at 22°C . into a glass-made reaction vessel of 100 ml capacity in such an amount that the pressure inside the vessel was about 10 Torr corresponding to a density of the compound molecules of 3.3×10^{17} molecules/ cm^3 and then air was introduced into the vessel to give a partial pressure of 155 Torr corresponding to a concentration of air of 5.7×10^{18} molecules/ cm^3 or an oxygen partial pressure of 31 Torr corresponding to an oxygen concentration of 1.1×10^{18} molecules/ cm^3 . The vapor mixture in the vessel was irradiated through the quartz glass-made window on the wall with a single pulse-wise flash of laser beams at a wavelength of 193 nm emitted from an ArF excimer laser. The pulse width was 10^{-8} second and the energy density was $5.0 \times 10^{-2} \text{ J}/\text{cm}^2$ to give an irradiation dose of 200 mJ. Deposition of fine particles was found on the wall of the vessel after emission of a very strong flash of light indicating an explosively rapid reaction taking place in the vapor phase. The thus obtained powder, weighing 9 mg, was lead oxide having a particle diameter not exceeding $0.5 \mu\text{m}$.

The results of this powdery product by the plasma-emission spectrophotometric analysis and CHN Coder indicated complete absence of the elements of carbon, hydrogen and nitrogen and the content of lead was 84% by weight. When the same experimental procedure as above was repeated excepting omission of introduction of air into the reaction vessel, the powdery product contained 98% by weight of lead. This difference in the content of lead is due to the formation of an oxide in the presence of the molecular oxygen. The X-ray photoelectron spectrophotometric analysis of the powdery product indicated a peak ascribable to oxygen O(1s) in the vicinity of 529.5 eV supporting the conclusion that this powdery product was an oxide of lead.

EXAMPLE 2

Vapor of trimethyl bismuth was introduced at 22°C . into a glass-made reaction vessel of 100 ml capacity in

300nm

such an amount that the pressure inside the vessel was about 20 Torr corresponding to a density of the compound molecules of 6.6×10^{17} molecules/cm³ and then air was introduced into the vessel to give a partial pressure of 140 Torr corresponding to a concentration of air of 4.6×10^{18} molecules/cm³. The vapor mixture in the vessel was irradiated through the quartz glass-made window on the wall with a single pulse-wise flash of laser beams at a wavelength of 193 nm emitted from an ArF excimer laser. The pulse width was 10^{-8} second and the energy density was 3.8×10^{-2} J/cm² to give an irradiation dose of 150 mJ. Deposition of fine particles was found on the wall of the vessel after emission of a very strong flash of light indicating an explosively rapid reaction taking place in the vapor phase. The thus obtained powder, weighing 25 mg, was bismuth oxide having diameter not exceeding 0.3 μ m.

The results of this powdery product by the X-ray photoelectron spectrophotometric analysis making reference to a standard sample of bismuth oxide Bi₂O₃ indicated good coincidence between the product and the standard to give the excitation energies of 158.7 eV and 158.5 eV, respectively, for Bi(4f 7/2) and 529.7 eV and 529.4 eV, respectively, for O(1s).

COMPARATIVE EXAMPLE 1

The experimental procedure was substantially the same as in Example 1 except that the energy density of the laser beam irradiation was 7.5×10^{-5} J/cm² and the irradiation dose was 0.3 mJ. No explosive chain reaction was noted in the vapor phase.

COMPARATIVE EXAMPLE 2

The experimental procedure was substantially the same as in Example 1 excepting replacement of the air introduced into the reaction vessel with pure nitrogen gas. No explosive chain reaction was noted in the vapor phase.

COMPARATIVE EXAMPLE 3

The experimental procedure was substantially the same as in Example 1 except that the concentration of the tetramethyl lead vapor was 3.3×10^{14} molecules/cm³ to give a partial pressure of 0.01 Torr. No explosive chain reaction was noted in the vapor phase.

EXAMPLE 3

Vapor of tetramethyl lead was introduced at 22° C. into a quartz glass-made cell of 7 ml capacity in a concentration of 3.3×10^{17} molecules/cm³ to give a partial pressure of 10.0 Torr and then vapor of methyl iodide was additionally introduced thereinto in a concentration of 6.4×10^{17} molecules/cm³ to give a partial pressure of 19.3 Torr. The vapor mixture in the cell was irradiated with a single pulse of laser beams having a wave length of 248 nm emitted from a KrF excimer laser. The pulse width of the beams was 1×10^{-8} second and the energy density of the incident laser beams was 75 mJ/cm² to give an irradiation dose of 300 mJ. Deposition of a fine yellow powder was found on the wall of the cell after emission of a very strong flash of orange light indicating an explosively rapid reaction taking place in the cell. The powdery product, weighing about 1.7 mg, had a particle diameter not exceeding 0.3 μ m.

This powdery product was subjected to the X-ray photoelectron spectrophotometric analysis to give the chart peaks at wavelengths of about 619.1 eV for iodine and about 138.5 eV for lead. The corresponding excita-

tion energies for a standard sample of lead diiodide PbI₂ were 619.0 eV and 136.4 eV, respectively. These values for lead are in good coincidence with value of 138.5 eV reported in Journal of Physical Chemistry volume 77, page 96 (1973) by W. E. Morgan et al. These results support the conclusion that the powdery product was lead diiodide.

EXAMPLE 4

Vapor of tetramethyl lead was introduced at 22° C. into a quartz glass made cell of 7 ml capacity in a concentration of 8.3×10^{17} molecules/cm³ to give a partial pressure of 25.0 Torr and then vapor of methyl bromide was additionally introduced thereinto in a concentration of 2.6×10^{18} molecules/cm³ to give a partial pressure of 77.9 Torr. The vapor mixture in the cell was irradiated with a single pulse of laser beams having a wave length of 193 nm emitted from an ArF excimer laser. The pulse width of the beams was 1×10^{-8} second and the energy density of the incident laser beams was 50 mJ/cm² to give an irradiation dose of 200 mJ. Deposition of a fine powder was found on the wall of the cell after a very strong flash of orange light indicating an explosively rapid reaction taking place in the cell. The powdery product, weighing about 2.8 mg, had a particle diameter not exceeding 0.3 μ m.

This powdery product was subjected to the X-ray photoelectron spectrophotometric analysis and the results were compared with those obtained with a commercially available sample of lead bromide to find good coincidence supporting the conclusion that this powdery product was lead bromide.

EXAMPLE 5

Vapor of tetramethyl lead was introduced at 22° C. into a quartz glass made cell of 7 ml capacity in a concentration of 8.3×10^{17} molecules/cm³ to give a partial pressure of 25.0 Torr and then vapor of methyl chloride was additionally introduced thereinto in a concentration of 1.6×10^{18} molecules/cm³ to give a partial pressure of 48.0 Torr. The vapor mixture in the cell was irradiated with a single pulse of laser beams having a wave length of 193 nm emitted from an ArF excimer laser. The pulse width of the beams was 1×10^{-8} second and the energy density of the incident laser beams was 50 mJ/cm² to give an irradiation dose of 200 mJ. Deposition of a fine powder was found on the wall of the cell after a very strong flash of orange light indicating an explosively rapid reaction taking place in the cell. The powdery product, weighing about 2.6 mg, had a particle diameter not exceeding 0.3 μ m.

This powdery product was subjected to the X-ray photoelectron spectrophotometric analysis and the results were compared with those obtained with a commercially available sample of lead dichloride to find good coincidence supporting the conclusion that this powdery product was lead dichloride.

EXAMPLE 6

The experimental procedure was substantially the same as in Example 3 excepting replacement of the tetramethyl lead with trimethyl bismuth. An explosive chain reaction took place in the cell to produce about 3.5 mg of a fine powder of bismuth iodide having a particle diameter not exceeding 0.3 μ m.

COMPARATIVE EXAMPLE 4

The experimental procedure was substantially the same as in Example 3 except that the energy density of the laser beam irradiation was 0.075 mJ/cm² instead of 75 mJ/cm² and the irradiation dose was 0.3 mJ instead of 300 mJ.

The results were that no explosive chain reaction took place in the cell.

COMPARATIVE EXAMPLE 5

The experimental procedure was substantially the same as in Example 3 except that the density of the tetramethyl lead was 3.3×10^{14} molecules/cm³ to give a partial pressure of 0.01 Torr instead of 3.3×10^{17} molecules/cm³.

The results were that no explosive chain reaction took place in the cell.

EXAMPLE 7

Vapor of tetramethyl lead was introduced at 22° C. into a glass-made reaction vessel of 100 ml capacity in such an amount that the pressure inside the vessel was about 15 Torr corresponding to a density of the compound molecules of 4.9×10^{17} molecules/cm³ and then vapor of trimethyl bismuth was introduced into the vessel to give a partial pressure of 5 Torr corresponding to a concentration of the compound of 1.6×10^{17} molecules/cm³. The vapor mixture in the vessel was irradiated through the quartz glass-made window on the wall with a single pulse-wise flash of laser beams at a wavelength of 193 nm emitted from an ArF excimer laser. The pulse width was 1×10^{-8} second and the energy density was 2.5×10^{-2} J/cm² to give an energy input of 100 mJ corresponding to 9.7×10^{16} photons. Deposition of fine particles was found on the wall of the vessel after a very strong flash of orange light indicating an explosively rapid reaction taking place in the vapor phase. The amount of the thus obtained powdery product was about 18 mg. The powder had a particle diameter not exceeding 5 μm and analysis of the same indicated that it was a composite metallic powder of lead and bismuth.

The same experimental procedure as above was repeated except that the mixing ratio of the tetramethyl lead vapor and trimethyl bismuth vapor was varied. When the concentrations of tetramethyl lead vapor and the trimethyl bismuth in the reaction vessel were 3.3×10^{17} molecules/cm³ to give a partial pressure of 10 Torr and also 3.3×10^{17} molecules/cm³ to give a partial pressure of 10 Torr, respectively, about 18 mg of a powdery product of composite metal particles having a particle diameter not exceeding 2 μm were obtained. When the concentrations of tetramethyl lead vapor and the trimethyl bismuth vapor in the reaction vessel were further varied to be 1.6×10^{17} molecules/cm³ to give a partial pressure of 5 Torr and also 4.9×10^{17} molecules/cm³ to give a partial pressure of 15 Torr, respectively, the amount of the powdery product of composite metal particles having a particle diameter not exceeding 1 μm was also about 18 mg.

The above described yields of the powdery product indicated that about 670 molecules of the organometallic compounds had been instantaneously decomposed into a metallic form by the irradiation with a single photon. This means that the energy efficiency in the inventive method is at least 700 times higher than in the conventional photochemical methods.

The particles of the composite metal powders obtained above were subjected to the examination of the distribution of the elements of lead and bismuth by using an electron probe microanalyzer (EPMA) to find that good coincidence was obtained between the distribution patterns of lead and bismuth. Further, the estimated relative contents of lead and bismuth in the particles were about the same as in the vapor phase. The EPMA photographs showed no particles composed of the single metal of lead alone or bismuth alone. These results support the conclusion that the composite metal powder obtained by the inventive method is very unique as compared with any composite metal powders obtained by conventional methods.

EXAMPLE 8

The experimental procedure was substantially the same as in Example 7 except that the vapor mixture in the reaction vessel was composed of tetramethyl lead vapor in a concentration of 3.3×10^{17} molecules/cm³ corresponding to a partial pressure of 10 Torr and tetramethyl tin vapor in concentration of 1.6×10^{17} molecules/cm³ corresponding to a partial pressure of 5 Torr. Deposition of a fine powder was found on the wall of the reaction vessel after a strong flash of orange light. The amount of the thus produced composite metal powder which had a particle diameter not exceeding 0.3 μm, was about 16 mg. The EPMA analysis of this composite metal powder indicated that the distributions of lead and tin were uniform throughout all of the particles and the ratio of the contents of these elements in the particles was about the same as in the vapor mixture. This is a very unique result in contrast to the general understanding that tetramethyl tin is hardly susceptible to a chain-like decomposition reaction by a single pulse irradiation with laser beams.

COMPARATIVE EXAMPLE 6

The experimental procedure was substantially the same as in the first experiment of Example 7 except that the energy density of the incident laser beams was 2.5×10^{-2} mJ/cm² to give an energy input of 0.1 mJ. No chain reaction for the decomposition of the organometallic compounds took place in the vapor mixture.

COMPARATIVE EXAMPLE 7

The experimental procedure was substantially the same as in Example 7 except that the vapor mixture in the reaction vessel was composed of tetramethyl lead vapor in a concentration of 3.3×10^{14} molecules/cm³ corresponding to a partial pressure of 0.01 Torr and trimethyl bismuth vapor in a concentration of 3.3×10^{14} molecules/cm³ corresponding to a partial pressure of 0.01 Torr. No chain reaction for the decomposition of the organometallic compounds took place in the vapor mixture.

COMPARATIVE EXAMPLE 8

The experimental procedure was substantially the same as in Example 7 except that the vapor mixture in the reaction vessel was composed of tetramethyl tin having a ΔH of 30 kcal/mole in a concentration of 4.9×10^{17} molecules/cm³ corresponding to a partial pressure of 15 Torr and tetramethyl germanium having a ΔH of 65 kcal/mole in a concentration of 1.7×10^{17} molecules/cm³ corresponding to a partial pressure of 5 Torr. No chain reaction for the decomposition of the

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organometallic compounds took place in the vapor mixture.

What is claimed is:

1. A method for the preparation of a metal oxide in a fine particulate form which comprises the steps of: 5

(a) admixing a vapor of an exothermically decomposable organometallic compound having a density of the molecules of the compound of at least 10^{15} molecules per cm^3 in the vapor phase with oxygen, air or an oxygen-containing compound in gaseous form capable of reacting with the organometallic compound to form a mixture in the vapor phase, wherein the concentration of said oxygen-containing compound in the vapor phase is at least equimolar to the organometallic compound calculated as molecular oxygen (O_2); and 10

(b) irradiating at least a pair of the vapor phase with laser beams in a pulse having a width not exceeding 15

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1×10^{-3} second, and having an energy density of at least 10^{-4} joules per cm^2 so as to produce activated species of the organometallic compound which starts an exothermic chain reaction of the organometallic compound with oxygen, air or the oxygen-containing compound to form the fine particles of metal oxide.

2. The method for the preparation of a metal oxide in a fine particulate form as claimed in claim 1 wherein the organometallic compound is an alkylated compound of the metallic element.

3. The method for the preparation of a metal oxide in a fine particulate form as claimed in claim 1 wherein the oxygen-containing compound is selected from the group consisting of oxygen, air, nitrous oxide, nitrogen monoxide, nitrogen dioxide and sulfur dioxide.

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United States Patent [19]**Rostoker**[11] **Patent Number:** **5,300,130**[45] **Date of Patent:** **Apr. 5, 1994**[54] **POLISHING MATERIAL**[75] **Inventor:** David Rostoker, Sturbridge, Mass.[73] **Assignee:** Saint Gobain/Norton Industrial
Ceramics Corp., Worcester, Mass.[21] **Appl. No.:** 96,804[22] **Filed:** Jul. 26, 1993[51] **Int. Cl.³** C09C 1/68[52] **U.S. Cl.** 51/309; 106/6[58] **Field of Search** 51/309; 106/6[56] **References Cited****U.S. PATENT DOCUMENTS**

4,657,754	4/1987	Bauer et al.	423/625
5,114,437	5/1992	Takenuchi et al.	51/309
5,149,338	9/1992	Fulton	51/309

Primary Examiner—Mark L. Bell*Assistant Examiner*—Willie J. Thompson*Attorney, Agent, or Firm*—David Bennett[57] **ABSTRACT**

A novel polishing slurry for particularly hard materials such a silicon carbide has been found. The slurry comprises diamond particles with a median particle size of around a micron and alpha alumina particles with a median size of from about 20 to about 200 nanometers.

10 Claims, No Drawings

POLISHING MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to polishing materials particularly to polishing materials based on diamond that are used to produce fine finishes on hard materials.

Certain very hard ceramic materials are extremely difficult to polish to a fine finish unless a diamond polishing slurry is employed. Such materials include for example silicon carbide, aluminum/titanium carbide, tungsten carbide, aluminum nitride and alpha alumina monolith bodies. Diamond is very expensive and thus the polishing process itself is very costly.

Typical diamond slurries for this application contain diamond particles less than 2 microns in diameter and contain from about 10 to about 20 carats per liter of the diamond. The diamond particles need to be kept in suspension and this is typically done using suspending agents. U.S. Pat. No. 5,149,338 however teaches the use of a colloidal boehmite to maintain a diamond abrasive powder in suspension. This is said to yield a finish below 20 angstroms RMS when used on silicon carbide at a pH of 4. The boehmite has no significant abrasive qualities and is merely a means of presenting the diamond particles to the surface in a more efficient way. Moreover the pH used is severely corrosive of all but the best quality stainless steel, (or other resistant material), for the equipment contacted by the slurry. Other materials are available for polishing such hard ceramics including colloidal silica but while these are undoubtedly cheaper than diamond they are generally less effective and take much longer to achieve an acceptable finish.

There is therefore a need for a cheaper alternative to diamond for polishing hard materials that does not have a deleterious effect on the equipment used. This need is filled by the present invention which is more effective than diamond used alone and yet is quicker to achieve its desired surface finish. While not so cheap as colloidal silica it is substantially less expensive than a pure diamond polishing slurry.

DESCRIPTION OF THE INVENTION

The present invention provides an aqueous polishing slurry comprising diamond particles having a median particle size of less than 5 microns and alpha alumina particles with an average particle size of from 20 to 200 nanometers with a diamond to alumina weight ratio of from about 1:30 to about 1:90. Advantageously the slurry also comprises a suspending agent to maintain the dispersion of the diamond component.

The diamond component is a conventional polishing material as used in the prior art but need be used in much lower amounts than in conventional polishing slurries. These would typically comprise two to five grams of the diamond per liter of polishing slurry. The preferred slurries of the invention comprise less than 2 grams, and conveniently from about 0.5 to about 1.5 gram of the same diamond per liter.

The alpha alumina component of the invention is a very finely divided material, and preferably one with a relatively narrow particle size distribution, for example one in which less than 5 volume percent of the particles have a size that is two or more times the volume average particle size of the alumina. Such materials can conveniently be obtained by the process described in U.S. Pat. No. 4,657,754. This process involves forming a sol of a hydrated alumina, adding a seed suitable for

the promotion of nucleation of the conversion of transition alumina to alpha alumina. Suitable seed include alpha alumina itself and other materials isostructural with alpha alumina and with lattice parameters closely related to those of alpha alumina, such as alpha ferric oxide, chromium oxide (in the Cr_2O_3 form) and various oxides and mixed oxides of titania. The sol of hydrated alumina can be gelled before or after the seed particles are added. The gelation can be done by acid peptization or by reducing the water content. Thereafter the gel is dried and then fired to a temperature and for a period to convert most of the alumina to alpha alumina but insufficient to cause significant sintering of the alpha alumina particles to occur. This resulting product is relatively easily milled to a powder of the desired particle size and size distribution. Thus the preferred alumina powder is a seeded sol-gel alpha alumina.

DETAILED DESCRIPTION OF THE INVENTION

The preferred polishing compositions of the invention are in the form of slurries comprising from about 0.8 to about 1.5 grams per liter of diamond particles with a median particle size of from about 0.5 to about 2.5, and more preferably from about 0.8 to about 1.5 micron. These preferred slurries also comprise from about 40 to about 80 grams per liter of an alpha alumina having a median particle size of from about 20 to about 200, and more preferably from about 40 to 100 nanometers. These alpha alumina particles are preferably produced by a seeded sol-gel process and may contain a minor amount, such as up to about 25% but preferably less than about 10%, by weight, of a transitional alumina such as gamma alumina.

The polishing slurry also preferably contains a suspending agent in an amount that is effective to maintain the diamond particles in suspension. There are many known commonly available suspending agents which are capable of performing this function such as xanthan gum, magnesium aluminosilicate clays, certain acrylic polymers and carboxymethyl cellulose. The effective amount will of course vary with the agent used. Generally an effective amount for xanthan gum is about 1 to 5 grams per liter for the amounts of diamond that are preferably involved.

In addition the slurry can contain other additives with specific functions not related to the abrasive performance such as bactericides and in some cases buffers. Unlike some of the prior art slurries, the pH of the compositions of the present invention is preferably maintained above 7 and often about 10. This avoids the corrosive problems of working at acid pH values that characterize some of the prior art slurries.

One significant advantage of the slurries of the invention is that they can be recycled until the swarf build-up renders them ineffective. In normal use, this can take as long as two to three weeks.

The slurries of the invention can be used with any conventional type of lapping pad or pitch lap. However the best results are often obtained using a pad that is relatively hard such as a polyurethane pad filled with glass beads and sold by Rodex Corporation under the trade designation IC-60. The slurries of the invention can be used to polish in either a single side or a double sided mode.

The applied weight on the pad during polishing can be in the range that is conventionally used for such

applications. However pressures at the higher end of the normal range can be used without detriment and this results in a faster cycle time without significant loss of surface quality.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention is now described with reference to the following examples which are for the purpose of illustration only and are not intended to imply any necessary limitation of the essential scope of the invention.

TABLE 1

Descrip.	Exp. #1	Exp. #2	Exp. #3	Exp. #4	Exp. #5	Exp. #6	Exp. #7	Exp. #8
Lapping Material	Pit.	Pit.	Pit.	IC 60	IC 60	IC 60	IC 60	IC 60
Pol. Ag.	B + D	B + D	B + D	A + D	A + D	A + D	A + D	A
AL Size	200 Ang.	30 nM	30 nM	30 nM	30 nM	1.0 Micr.	30 nM	30 nM
AL Vol.	4 oz	4 oz	4 oz	250 ml/l	250 ml/l	250 ml/l	250 ml/l	250 ml/l
AL %	17%	17%	17%	22%	22%	22%	22%	22%
Solids								
D. Size	2-4	2-4	2-4	1	1	1	1	
D. Conc (ct/l)	2.5	2.5	2.5	1.0	16	5	4	
Weight (lbs)	5	5	5	46.5	46.5	46.5	46.5	46.5
Time hours	2	—	4	1.5	.75	1.5	.75-1.0	1.5
Finish	10/90	—	0/35	5/80	5/40	40/550	5/35	150/1000
RMS/TIR								
Water Amnt.	4 oz.	4 oz.	4 oz.	750 ml + Gum	750 ml + Gum	750 ml + Gum	750 ml + Gum	750 ml + Gum

EXAMPLE 1

The purpose of this Example is to demonstrate the improvement represented by the slurries of the present invention over the art as represented by the sole Example contained in U.S. Pat. No. 5,147,338 (discussed above).

Run #1 is a replication, in different equipment, of the Example in the above patent using all other conditions as specified therein. Run #2 was the same as Run #1 except that the alumina particle size was changed from 200 angstroms to 30 nanometers. Run #3 repeated Run #2 except that xanthan gum was added to keep the diamond in suspension. It will be noted from the results that in Run #2 the absence of the suspending boehmite that was present in Run #1 had disastrous results.

Runs #4, #5 #6 and #7 are according to the invention and show the effect of varying the amount of diamond and the particle size of the alumina. Comparison of Runs #5 and #7 show that there is little or no benefit from quadrupling the amount of diamond, and Run #6 shows that increasing the alumina particle size to an average particle size of one micron has a very negative effect on the performance. Run #8 duplicates Run #7 but without the diamond component. As can be seen the excellent properties of the compositions of the invention are not obtained using the alumina component alone.

In Table 1 below the following abbreviations are used: "A" is alpha alumina, "B" is boehmite and "D" is diamond. "Pit." is a commercial pitch available from Gugolz GmbH of Winterthur, Switzerland under the designation "CH84-04". This is similar to pitch used in U.S. Pat. No. 5,149,338 as the polishing tool. "Weight" is the applied load on the polishing tool. "Time" is the time taken to achieve the indicated finish. "RMS" is the calculated average amplitude of the peaks and valleys

over an 80 micron traverse of a diamond stylus across the surface.

The units are angstroms. "TIR" is the greatest peak-to-valley distance, in angstroms, measured during the traverse that yielded the RMS result. Both RMS and TIR were measured using a "Tencor Alpha-Step 200" available from the Tencor Corporation.

The "Gum" added during the Experiments that exemplified the invention was xanthan gum and was used to keep the diamond in suspension.

Except for #1, where the pH was 4, the pH was maintained at 10.05

From the data in the above Table it is clear that the process of the prior art patent is not capable of yielding improved results merely by making the boehmite particles larger, indeed the results were so bad in Exp. #2 that no values could be obtained for the finish. Nor was the addition of gum the answer for although a good finish was obtained, it took four hours to obtain it.

The data in the Table also show that excellent results are obtained in a very short time using alpha alumina but that the results deteriorate drastically, (Expt #6), if the alpha particle size becomes comparable to that of the diamond component.

EXAMPLE 2

This Example shows the utility of the compositions of the invention in the polishing of a number of very hard materials in comparison with diamond used alone.

In each case the diamond component had the same size, (about one micron) and was used in the same quantity, (5 ct/l). The alpha alumina used had a median particle size of 50 nanometers and was used in a concentration of 66 gram/liter. In each case the same amount of xanthan gum was used to maintain the dispersion of the components.

The results appear in Table 2 below.

TABLE 2

Material	Polish	Time Hr.	RMS	TIR
SiC (Hot Press)	D/A	1.0	5	35
SiC (Hot Press)	D	1.0	15	70
Al TiC	D/A	1.0	7	60
Al TiC	D	1.5	10	70
WC	D/A	.5-.75	5	50
AlN	D/A	1.5	140	700
IBM Alumina	D/A	2	165	1000

TABLE 2-continued

Material	Polish	Time Hr.	RMS	TIR
CPS Alumina	D/A	1	225	1600

The abbreviations "D", "A", "RMS" and "TIR" are as explained for Table 1 and the RMS and TIR units are angstroms. The aluminum nitride, (AlN), contains a higher proportion of binder that leads to significant grain "pull-out" during polishing. This is also true of the IBM and CPS aluminas polished. Both are fully fired aluminas with about 10 to 15% of a binder.

These results clearly demonstrate that the diamond-/alumina compositions of the invention possess a striking synergistic effectiveness that is not matched by either component alone.

What is claimed is:

1. A polishing slurry comprising diamond particles having a particle size less than 5 microns, alpha alumina particles with an average particle size of from 20 to 200 nanometers and an amount of a suspending agent effective to maintain the diamond particles in suspension; the slurry having a diamond to alumina weight ratio of from about 1:30 to about 1:90.

2. A polishing slurry according to claim 1 in which the diamond particle have a median particle size of from about 0.5 to about 1.5 micron.

3. A polishing slurry according to claim 1 in which the alpha alumina particles have a median particle size of from about 40 to 5 about 100 nanometers.

4. A polishing slurry according to claim 1 in which the diamond to alumina weight ratio is from about 1:50 to about 1:80.

5. A polishing slurry according to claim 1 in which the solids content is from about 40 to about 80 grams per liter.

6. A polishing slurry according to claim 1 in which the suspending agent is xanthan gum.

7. A polishing slurry according to claim 6 in which the amount of the xanthan gum is from about 1 to about 5 gm/l.

8. A polishing slurry comprising from about 1 to 10 carat/liter of diamond particles having a median particle size of from about 0.2 to about 1.0 micron, from about 30 to about 90 grams/liter of alpha alumina particles with an median particle size of from about 40 to about 100 nanometers and an amount of a suspending agent effective to maintain the diamond particles in suspension; the slurry having a diamond to alumina weight ratio of from about 1:40 to about 1:80.

9. A polishing slurry according to claim 8 in which the suspending agent is xanthan gum.

10. A polishing slurry according to claim 9 which comprises from about 1 to about 5 gm/liter of xanthan gum as the suspending agent.

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US005417956A

United States Patent [19]

Moser

[11] Patent Number: **5,417,956**[45] Date of Patent: **May 23, 1995****[54] PREPARATION OF NANOPHASE SOLID STATE MATERIALS**

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[73] Assignee: Worcester Polytechnic Institute,
Worcester, Mass.

[21] Appl. No.: 931,765

[22] Filed: Aug. 18, 1992

[51] Int. Cl.⁶ C01B 13/36[52] U.S. Cl. 423/592; 423/263;
423/593; 423/598; 423/608; 423/625; 423/632;
423/636[58] Field of Search 423/592, 593, 598, 608,
423/636, 625, 263, 632**[56] References Cited****U.S. PATENT DOCUMENTS**

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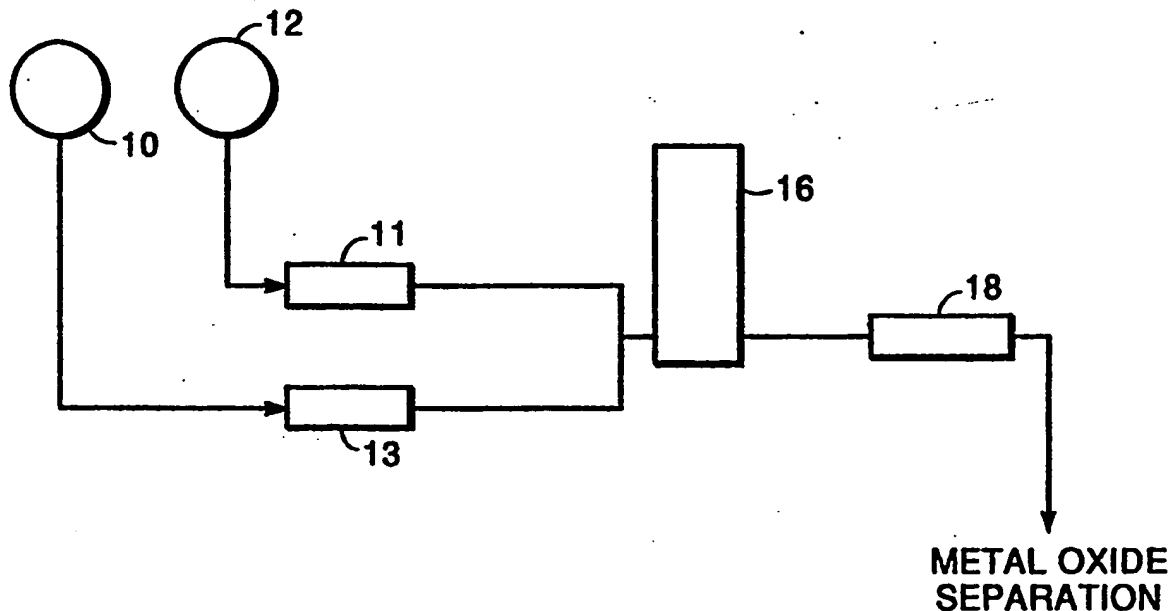
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Primary Examiner—Wayne Langel*Attorney, Agent, or Firm*—Bruce F. Jacobs**[57]****ABSTRACT**

A process for the preparation of nanophase solid state materials having crystallite morphology and particle sizes in the range of from about 1 nm to 30 nm is disclosed. Novel nanophase solid state materials are also disclosed.

19 Claims, 4 Drawing Sheets

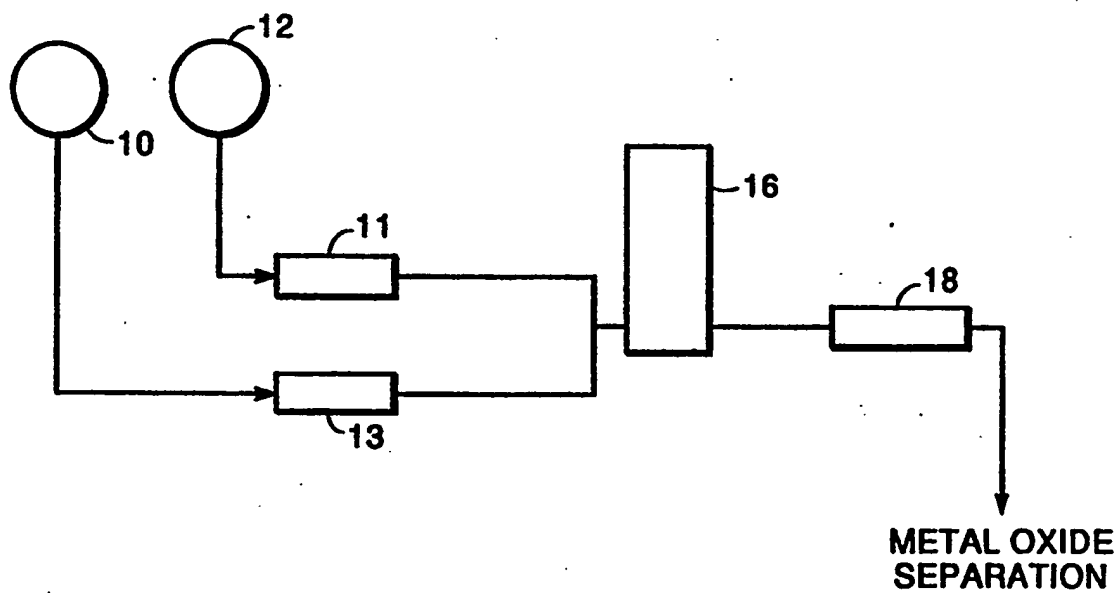


FIG. 1

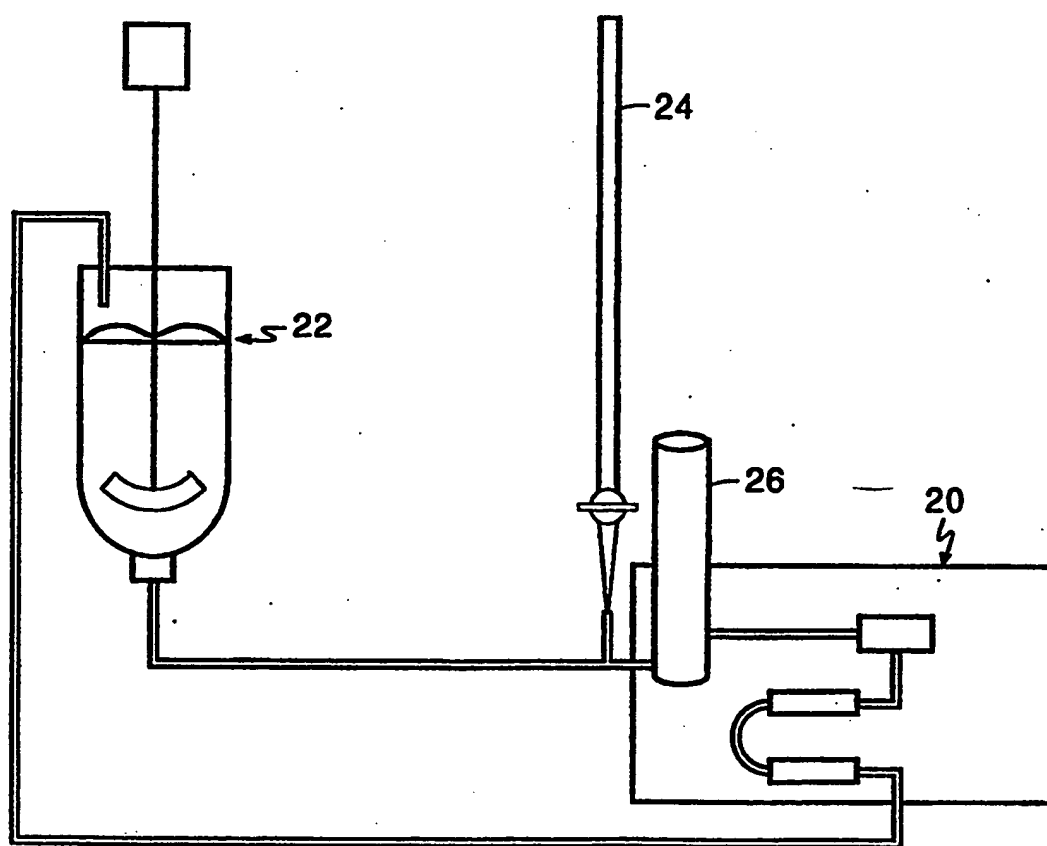


FIG. 2

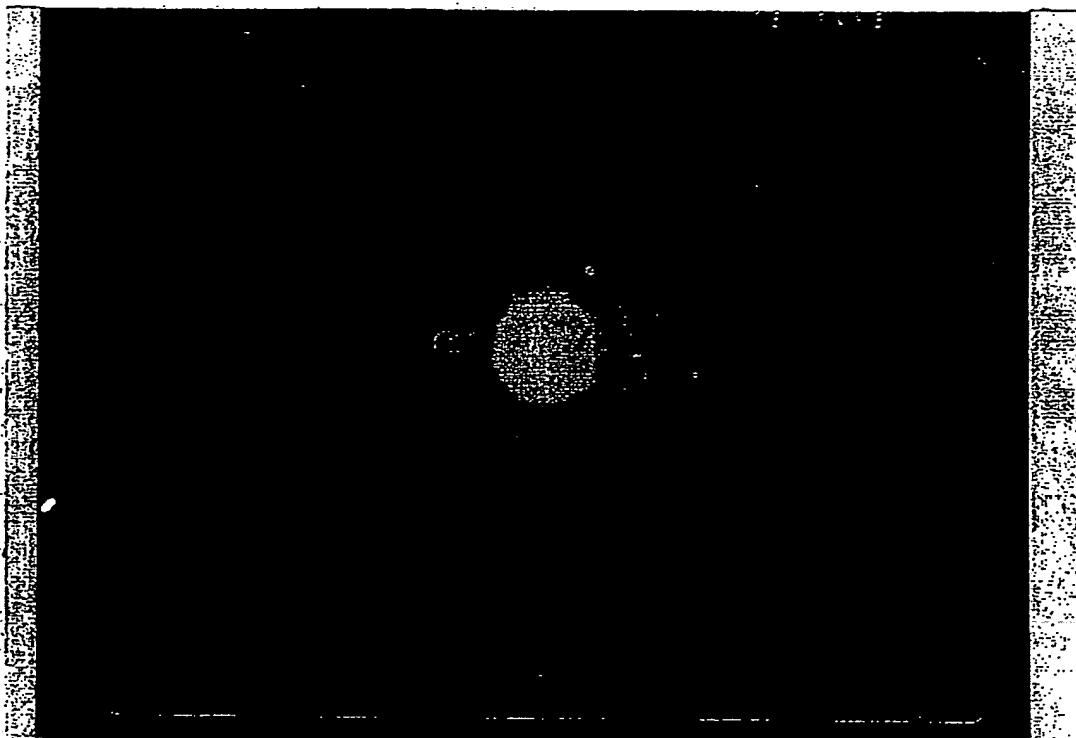


FIG. 3



FIG. 4

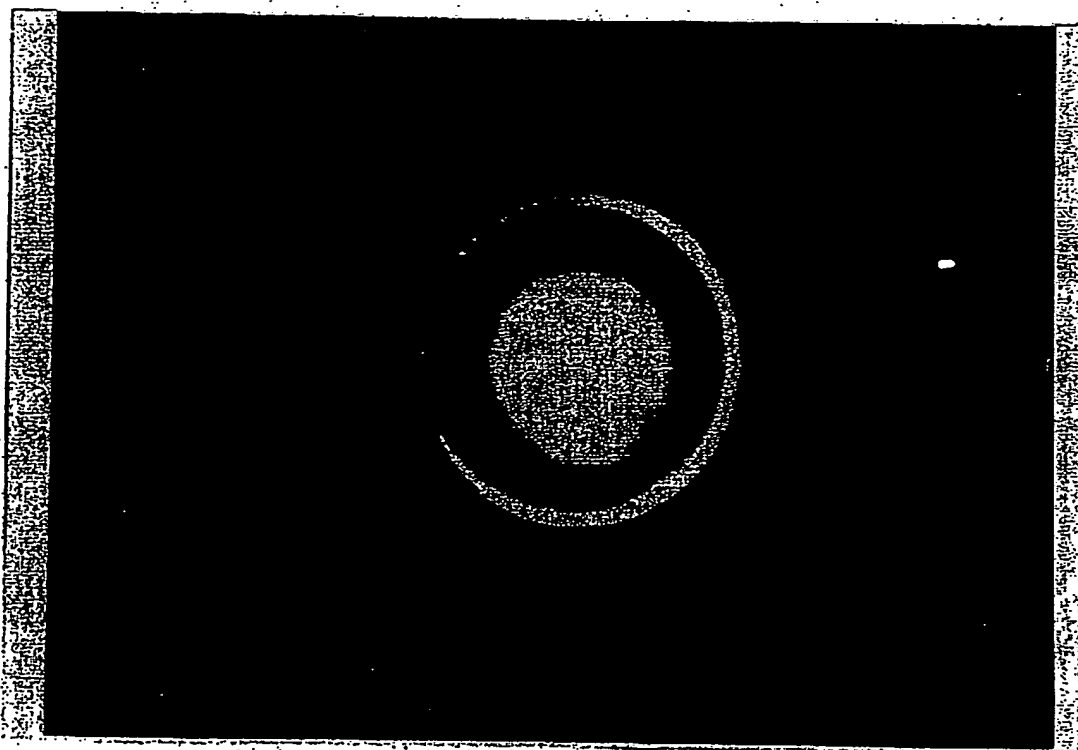


FIG. 5

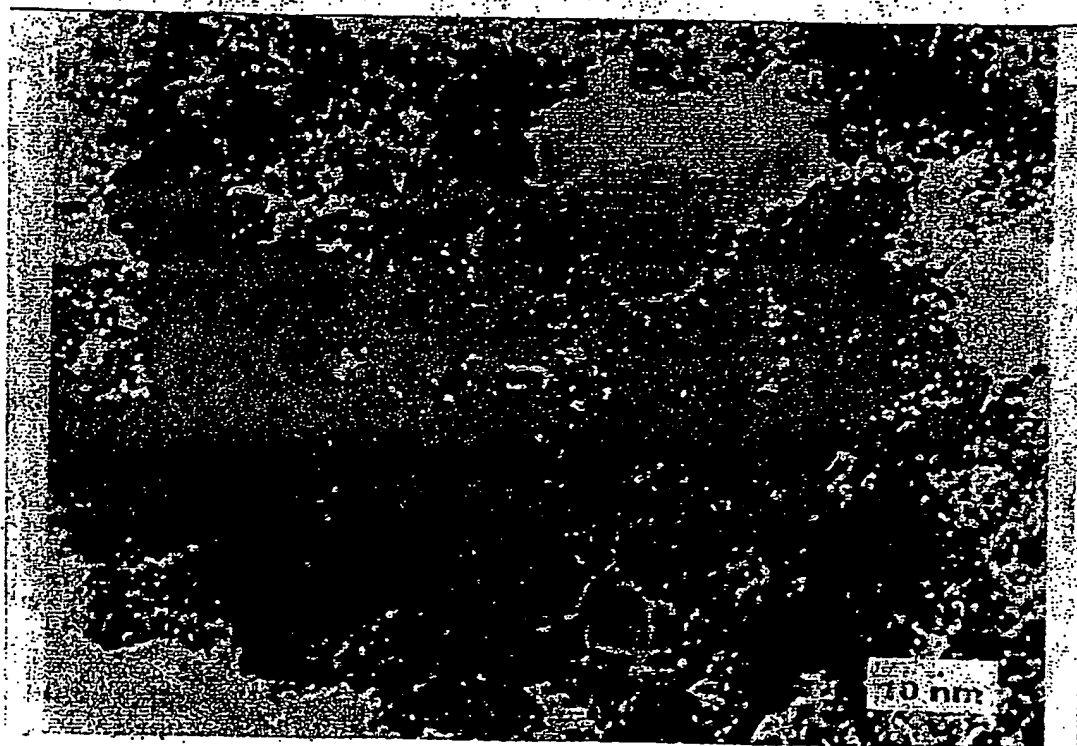


FIG. 6

PREPARATION OF NANOPHASE SOLID STATE MATERIALS

BACKGROUND OF THE INVENTION

Nanophase materials composed of nanosize particles are used in a variety of applications to produce a variety of products. The ceramic industry frequently utilizes nanophase solid state materials to produce ceramic based products. Nanosize materials are also useful in forming thin coatings for electronic and superconducting applications. Other uses of nanophase solid state materials include catalysts, superconductors and oxides for recording media. Such nanophase materials are particularly useful in these and other applications because they can be densified by various techniques resulting in high strength materials and materials containing a relatively high percentage of the densified material. Nanophase materials are also useful in the fabrication of electronic devices since small particles calcine at lower temperatures to form continuous structures.

Co-precipitation processes are normally employed to manufacture such nanophase materials. The co-precipitation method, however, has the disadvantage of producing materials which are not exceptionally homogeneous and the reproducibility of the process is often poor and it is not a general process for the synthesis of nanophase materials. In addition, the materials produced by the conventional co-precipitation require relatively higher calcination temperatures to cause densification. Higher calcination temperatures are disadvantageous because they lead to higher defect concentrations resulting in decreased resistance to fracture. Gas phase processes have been used for synthesizing a few nanophase compounds. These processes are usually not suitable for general metal oxide syntheses. Moreover, production rates are very low.

As a result, there is a need for a process to synthesize such materials generally which is both easily reproducible and which provides nanophase solid state materials for use as ceramics, catalysts, superconductors, electronic part coatings, and the like.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a process for producing nanophase solid state materials such as metal and metal oxide based materials, which is easily reproducible and results in materials having crystallite morphologies and particle sizes in the nanosize range of from about 1 to 30 nanometers. The process generally comprises (1) mixing together a metal solution such as a metal salt solution and a solution containing a precipitating agent to form a mixed solution, (2) pressurizing the mixed solution, (3) passing the pressurized mixed solution into a fluidizer apparatus wherein high shear forces act on the mixed solution creating solid state materials having nanosize particles, (4) depressurizing the mixed solution so as to cause cavitation and (5) separating a nanophase solid state material from the cavitated mixed solution. Preferably, the pressures must be maintained at a pressure greater than about 18,000 psi.

The process according to the present invention preferably employs a special apparatus to carry out steps 3 and 4 in the process such as a Microfluidizer, manufactured by Microfluidics Corporation of Newton, Mass. By controlling the pressure of the mixed solution before it is subjected to high shear forces in the fluidizer appa-

ratus, the particle size of the nanophase solid state materials which are finally produced can be controlled. By increasing the pressure to about 1,000 to 50,000 psig, preferably greater than about 18,000 psig, and more preferably to about 25,000 to 50,000 psig, the particle size of the solid state materials within the mixed solution are reduced facilitating homogeneous distribution of the various metals within the solid state materials. Moreover, as a result of the cavitation that occurs, thermal calcining, which is normally carried out as a separate step in a co-precipitation process, occurs in situ when the pressures are relatively high of from about 18,000 to 50,000 psig.

The process according to the present invention is particularly suitable for producing nanophase solid state materials such as metal oxides for use as coatings in electronic and superconducting applications and as ceramic materials. Such materials can be economically manufactured in large quantities and can be densified to their maximum density at much lower calcination temperatures (100° C.-150° C.) than classically prepared materials whose crystallite sizes are much larger in the range of about 0.1 microns. The lowering of the calcination temperature is variable and very much dependent on the metal oxide being calcined.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a process scheme for an embodiment of the present invention.

FIG. 2 is a process scheme of another embodiment of the present invention.

FIGS. 3-5 are electron diffraction patterns of FeO (FIG. 3), MgO (FIG. 4) and titanium oxide (anatase) (FIG. 5).

FIG. 6 is a TEM picture of TiO₂ (anatase) at a magnification of 200,000.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawings, one embodiment according to the present invention, a continuous process, is shown in FIG. 1. As shown, a metal containing solution such as a metal salt solution within reservoir 10 and a solution containing a precipitating agent within reservoir 12 are passed through metering pumps 11 and 12 respectively and then together forming a mixed solution just prior to entry into a high pressure pump 16. The precipitating agent solution must be maintained at a suitable pH to facilitate the precipitation of the metal ions in solution. Depending upon the metal solution and the precipitating agent, the pH generally is of from about 7.5 to 12. While pump 16 is shown outside fluidizing apparatus 18, it may be disposed within the apparatus. The mixed solution passes through the high pressure pump 16 and elevated by the action of the pump to a pressure of from about 1,000 to 50,000 psig, preferably more than 18,000 psig, and more preferably to a pressure of from about 20,000 to 50,000 psig. The pressure employed will depend upon the end product and the particle size which is desired. Generally, as the pressure is increased the particle size of the metal components is decreased.

The mixed solution at a high pressure is then channeled into fluidizing apparatus 18. Within apparatus 18 the mixed solution is vigorously mixed. This preferably takes place within the apparatus by dividing the mixed solution into two streams and then recombining the two

streams by redirecting them so that they collide with each other. At the point of the collision, the mixed solution undergoes vigorous mixing and high shear while and high shear simultaneous returning to atmospheric pressure. As the pressure drops rapidly from above about 1,000 psig to atmospheric pressure, bubbles form within the mixed solution and thereafter rapidly collapse releasing energy. The energy released when the bubbles collapse, known as cavitation, is transferred to the precipitated metal material suspended within the liquid. This rapid heat up followed by a rapid local cooling as the energy is released results in an effective high temperature calcining of the solid metal materials formed while they are in a high state of dispersion. The desired solid metal materials are then removed from solution by suitable separation techniques. Such techniques include vacuum filtration, filtration and evaporation. Filtration is generally not desirable because of the nanometer particle sizes of the nanophase solid state materials so formed. Rather evaporation of the water or solution liquid leaving the highly dispersed solid metal materials is the preferred method of separation. The materials are then dried by suitable means. In most cases, the nanophase solid metal materials are ready for use, without the need for calcining as a result of the cavitation that occurs in apparatus 18. Normally, additional calcining is not required when pressures above about 20,000 psi are employed during processing.

While any suitable apparatus may be used to achieve the vigorous mixing and cavitation, a particularly preferred device is the device disclosed in U.S. Pat. No. 4,533,254, which is incorporated herein by reference. A particularly preferred apparatus is the Microfluidizer, manufactured by Microfluidics Corporation of Newton, Mass.

Another embodiment according to the present invention is shown in FIG. 2. In this embodiment a recirculation line is added to recirculate the mixed solution which has been treated in fluidizer apparatus 20. As shown, a metal salt solution disposed in reservoir 22 (Port A) is circulated and mixed with a solution containing a precipitating agent stored in reservoir 24. The two solutions are initially mixed at Port B just prior to entering a high pressure pump 26 disposed in fluidizer 20. The fluidizer apparatus 20 operates in the same manner as fluidizer apparatus 18 in FIG. 1. After undergoing vigorous mixing and cavitation in the fluidizer 20, the mixed solution is recirculated through reservoir 22. The mixed solution continues to circulate undergoing treatment within the fluidizer while the precipitating agent is gradually added generally over a period of about 30 to 40 minutes. This time can vary over this range and even outside of the range depending upon the amount of materials being mixed. The recirculation generally continues for about 10 to 40 minutes and more preferably from about 20 to 40 minutes after the complete addition of precipitating agent. The period of recirculation will depend upon the final product and desired particle size which is desired and can vary outside of the general range recited herein. The longer the period of recirculation normally translates into a final product which has a high degree of phase purity, and smaller particle size.

In another embodiment (not shown), which is presently preferred, the reservoir 22 of FIG. 2 contains precipitating agent solution and the reservoir 24 contains the metal salt solution for addition to the recirculating line. This embodiment operates in the same manner as the FIG. 2 embodiment except for the reversal of

the two reservoirs. This embodiment is presently the most preferred because precipitated nanophase solid state material is recirculated so that particle sizes are further reduced during recirculation, and additional high temperature calcining is realized.

In still another embodiment, the metal salt solution and the precipitating agent solution may be premixed in a single reservoir and then passed through a pressurizing pump and then into the fluidizing apparatus. This embodiment may be employed either with or without recirculation, although recirculation is preferred to achieve nanosize materials. The first pass through mainly produces the nanophase particles, recirculation provides break up of loose agglomerates and gives additional calcining.

In certain situations; particularly when employing the process to make mixed metal oxide catalysts, it is sometimes necessary to use separate reservoirs to store the different metal salt solutions. This is because particular metal salts need particular solvents in which to be dissolved. Accordingly, different reservoirs with different solvents are required to dissolve the different metal salts. In such a situation the separate metal salt solutions are combined with the precipitating agent solution just prior to the pressurizing pump.

To synthesize the nanophase solid state materials as described herein, specific stoichiometries are required for each preparation. Generally, the metal solution stoichiometry is the same as the desired solid state metal stoichiometry.

In the embodiments where the precipitating agent is recirculated, it is desirable that the pH of the mixed solution be maintained on the basic side; i.e.; between about 7.5 to 12 and more preferably between about 8.5 to 12. However, the range is dependent on the precise solid state metal synthesized. In some cases, additional precipitating agent must be added to the recirculating mixed solution to keep the pH in the high range of about 8 to 12. In the case where the metal solution is recirculated and the precipitating agent added just before the pump, a total amount of precipitating agent is added so that the pH of the recirculating mixed solution rises slowly into the range of about 8-12.

The invention process is particularly useful in making nanophase solid state metal based materials such as metal oxides. In making such products, the metal which makes up the products are added in the form of one or more metals dissolved in a solution. Most metals are in the form of salts. However in the case of certain precious metals the metal may be added in the form of an acid such as chloroplatinic acid. Examples of suitable salts include nitrates, sulfates, acetates, chlorides, bromides, hydroxide, oxylates and acetylacetonates. The particular metals will, of course, depend on the particular product which is being made. For example, if the desired solid state material is barium titanite, a suitable metal salt solution comprises barium acetate in water and titanium tetraisopropoxide in isopropyl alcohol. In the case of zirconia, a suitable metal salt solution is zirconyl nitrate in water and a ceramic such as alumina uses aluminum nitrate. A metal oxide such as iron oxide uses metal salts such as ferric nitrate hydrate. A ceramic such as lanthana can be made from lanthanum nitrate. Magnesium oxide can be made using a metal salt solution such as magnesium nitrate.

The solutions into which the metal salt is dissolved will depend upon the particular metal salt. Suitable liquids include water, aqueous nitric acid, alcohols,

acetone, hydrocarbons, chlorinated hydrocarbons, and the like.

The precipitating agent may be selected from any suitable basic material such as sodium carbonate, ammonium carbonate, potassium carbonate, ammonium hydroxide, substituted ammonium hydroxides, alkali metal hydroxides, and other basic materials which are dissolved in water or water by itself if the metal salt spontaneously reacts with water.

The products produced by the process of the invention have components which are highly dispersed throughout the composition resulting in superior phase purity as compared to the same product produced by the prior art processes. The nanophase products are composed of nanosize particles ranging in size of from about 1 to 1,000 nm, more preferably of from about 1 to 30 nm, still more preferably of less than about 10 nm, and most preferably of from about 0.1 to 3 nm. The morphology of the particles varies depending upon the material produced and can range from interlaced crystals to mixed irregular crystals to amorphous particles, thin disks (0.5 nm) and needles (10 nm).

Examples of nanophase materials according to the present invention include barium titanate, zirconia, magnesia, iron oxide, lanthana, alumina, and titania. These materials have particle sizes in the nanometer range of from about 1 to 30 nm and are crystalline.

The following Examples more specifically described the nanophase solid state materials of the present invention and the novel process of the present invention used to make such materials. These Examples discuss the electron diffraction and TEM patterns with reference to the figures showing the patterns. They also compare conventionally prepared materials with those prepared according to the process of the present invention.

EXAMPLE 1

All of the materials listed in Table II were synthesized using the process of the present invention by dissolving the appropriate salts in water and loading in the salt solution in reservoir 24 shown in FIG. 2. The salts used to make the final products are shown in Table I.

TABLE I

Final Product	Salt
Alumina	Aluminum nitrate
Barium titanate	Barium acetate in water and titanium isopropoxide in isopropanol
Cobalt Oxide	Cobalt Nitrate
Iron Oxide	Ferric nitrate
Lanthana	Lanthanum nitrate
Magnesium Oxide	Magnesium nitrate
Titania	Titanium isopropoxide in isopropanol
Zirconia	Zirconyl nitrate hydrate

The salt solution was then added over a period of 30 min to a recirculating solution into the microfluidizer of a basic ammonium hydroxide solution in water forming a mixed solution. The mixed solution was pressurized by pump 26 to a pressure of about 12,000 to 20,000 psig. The mixed solution then passed into the fluidizer 20 wherein it underwent cavitation. After addition of the salt solution, the recirculation was continued for 30 minutes. The resulting product was separated by evaporating the solvent on a rotary evaporator under a vacuum (pressure=40 torr).

The materials so synthesized were analyzed by XRD analysis and demonstrated no reflections at all indicating that they were either micro-crystalline, amorphous

or a mixture of both. They were also analyzed by Transmission Electron Microscopy (TEM), and selected area electron diffraction (SAD). The crystallite morphologies as determined by TEM and the crystallinity as judged by SAD for each of the materials produced are listed as follows:

TABLE II

MATERIAL	MORPHOLOGY	SIZE, nm	CRYSTALLINITY
Barium Titanate (BaTiO_3)	Agglomerated strands	3-30	Mixed crystalline mainly amorphous
Zirconia (ZrO_2)	Crystallite agglomerated strands	2-10	Mixed Crystalline and amorphous
Cobalt Oxide (CoO)	Disks 40-580	2-10	Crystalline
Magnesium Oxide (MgO)	Disks (thin)	10-60	Crystalline
Iron oxide (FeO)	Irregular	1-3 20 x 260	Crystalline Crystallites (about 5%)
Lanthana (La_2O_3)	Needles	1 x 60	Mixed crystalline and amorphous
Alumina	—	—	Amorphous but possible extremely small crystals
Titania (TiO_2)	Irregular	1-6 (Processed at 20,000 psi)	Crystalline

All materials gave distinct ring patterns from the selected area electron diffraction analysis. The samples of zirconium, cobalt, magnesium, iron, lanthanum and titanium oxides gave strong ring patterns. These ring patterns were compared to computer generated ring patterns which calculated the patterns based on the lattice parameters and structures for all known structures for each composition. This technique permitted the definitive identification of the materials synthesized as ZrO_2 (tetragonal or cubic), CoO (cubic), Fe_2O_3 (cubic), and TiO_2 (Anatase). This comparison between measured patterns and calculated patterns permitted the definite exclusion of FeO and Fe_3O_4 for the iron oxide, Co_2O_3 for the cobalt oxide, and TiO_2 (brookite) and TiO_2 (rutile) as possible structures for the titanium oxide. The barium-titanium oxides gave weak rings and moderately strong amorphous reflections as did the lanthanum oxide. However, these materials could be assigned to BaTiO_3 and La_2O_3 .

The selected area microdiffraction (SAD) patterns taken by TEM analysis for iron oxide are shown in FIG. 3 and for magnesium oxide in FIG. 4. These data demonstrate that the nanophase materials are crystalline. The ring pattern in the SAD analysis prove they are crystalline. The particle size and morphology were determined by TEM photographs taken at 100,000 magnification. Studies which produced TiO_2 at continuously increasing process pressures from 9,000 to 20,000 psi showed that, as the pressure increased the electron diffraction patterns for TiO_2 (anatase) became sharper and more distinct indicating a higher degree of nanophase micro-crystallinity. The TEM analysis over this pressure range showed the production of smaller particles as the pressure increased.

EXAMPLE 2

This examples illustrates the use of the process of the invention to synthesize ceramics as nanometer size micro-crystallites. It further demonstrates that through

increasing the intensity of the cavitation effect the high temperature phases may be obtained directly from the process without any post process calcination. In each of these experiments the intensity of the cavitation effect was adjusted (1) by increasing the pressure within the cavitation chamber and (2) by changing the commercial Microfluidizer device used to produce the cavitation from the larger to the smaller flow channel orifice.

This example demonstrates the production of titanium oxide in a range from moderate sized particles to the very fine, nanometer sized particles of this invention by adjusting the cavitation process conditions. In addition, other adjustments in the process conditions showed that a high temperature calcination could be effected in situ in the solution undergoing the cavitation effect resulting in a high temperature form of TiO_2 . The results of these syntheses were compared to classical co-precipitation preparations.

The process utilized 26.5 mL of titanium tetrabutoxide dissolved in 30 mL of hexane. This solution is reactive in air, and it was loaded into a burette in a dry box and protected from the atmosphere by a nitrogen atmosphere when load into the Microfluidizer at Port A shown in FIG. 2. Distilled water, 200 mL, containing 1 wt. % Tween, a commercial surfactant (Aldrich Chemical Company) was placed in the reservoir at Port B of FIG. 1, and this solution was circulated through the fluidizer at pressure of 20,000 psi. In this case the water of the solution rapidly reacts with the alkoxide to form TiO_2 . The titanium butoxide solution was added to the recirculating solution of 1.5-2.0 mL per minute. After the addition was completed, the solution was recirculated for 40 minutes. Two experiments were carried out at 20,000 psig but using two different flow channels of the Microfluidizer device in the cavitation generation section of the fluidizer. The solids produced in each instance were removed using 0.2 micron filter paper by repetitively passing the filtrate through a filter pad. Initially most of the solids passed through the filter. The final drying was done at room temperature and then heated at 80° C. for 10 hours.

The XRD of the material produced by use of the smaller flow channel orifice in the cavitation section of the fluidizer demonstrated very low intensity and broad reflections at diffraction angles consistent with the anatase form of TiO_2 . The transmission electron microscopic evaluation (TEM) is shown in FIG. 6 and indicates that the average particle size of the microcrystallites was 4.5 nanometers. The material was shown to be crystalline by the selected area microdiffraction (SAD) patterns of FIG. 5. Also an analysis of the electron diffraction ring pattern showed that reflections appeared at d-spacings of 3.48, 2.37, 1.93, 1.66, and 1.45 Å. The JCPDS file standard spectrum indicates that reflections at 3.52, 2.37, 1.89, 1.67, and 1.48 Å corresponds to the anatase form of TiO_2 . This method of cavitation processing yielded a high temperature form of titania, namely anatase, by adjusting the processing (Microfluidizer device operating) conditions.

The experiment using the larger flow channel orifice into the cavitation chamber also resulted in a microcrystalline titania phase as demonstrated by SAD analysis. However, the phase of the titania is unknown as it exhibited reflections at d-spacings of 3.26, 2.49, 2.00, 1.74, and 1.45 Å. The average particle size of the titania in this experiment was 10.0 nanometers.

Titania was synthesized in parallel experiments using classical methods of synthesis. In this synthesis, the same amounts and concentrations of reagents were used. The difference in the synthesis was that the titanium tetrabutoxide solution in hexane was added dropwise at the same rate as in the cavitation synthesis, but the addition was to the 1% Tween in water solution in a well-stirred reaction flask. The TEM analysis of this material showed that it was not microcrystalline, and the XRD pattern showed no reflections between 10 and 50 degree two theta. Thus an amorphous material was produced.

EXAMPLE 3

The same cavitation synthesis as described in Example 2 was performed except that the pressure within the cavitation chamber was varied, i.e. 9,000, 13,500, 18,000, and 20,000 psig. When the respective samples were analyzed by Scanning Electron Microscopy (SEM), it was observed that the particle size of the solid titania was gradually reduced as the cavitation process pressure was increased. The largest particles in the four preparations were 70 nm at 9,000 psig, 24-nm at 13,500 psig, 10 nm at 18,000 psig, and 5 nm at 20,000 psig. These particle sizes were those of agglomerated microcrystals. The agglomerate particle size at 20,000 psig using the smaller flow channel orifice in the cavitation chamber resulted in agglomerated particles of 0.2 nm. TEM analysis of the samples showed that the individual particles that make up the agglomerates decreased in size as the cavitation pressure was increased. XRD analysis of the samples resulting from this pressure series showed no discrete peaks at low pressures and low intensity broad peaks as the pressure increased. This synthesis series demonstrates that the particle size of cavitationally prepared materials may be altered in a controlled way through the adjustment of process parameters.

What is claimed is:

1. A process for producing nanophase solid state materials comprising (1) mixing together a metal containing solution and a second solution containing a precipitating agent to form a mixed solution, (2) pressurizing the mixed solution to a pressure of about 1,000 to 50,000 psig, (3) passing the pressurized mixed solution into a fluidizing apparatus wherein high shear forces act on the mixed solution, creating nanophase solid state materials having nanosize particles having average sizes of from about 1 to 30 nm, (4) depressurizing the mixed solution so as to cause cavitation and (5) separating the nanophase solid material from the cavitated mixed solution.
2. The process of claim 1, wherein the pressure is of from about 25,000 to 50,000 psig.
3. The process of claim 1, wherein the metal containing solution and the precipitating agent containing solution are mixed prior to passage into the fluidizing apparatus.
4. The process of claim 1, wherein the mixed solution is recycled through the fluidizer apparatus.
5. The process of claim 4, wherein the precipitating agent solution is added to the mixed solution as it is recycled.
6. The process of claim 4, wherein the metal containing solution is added to the mixed solution as it is recycled.

7. The process of claim 1, wherein the metal containing solution and the precipitating agent solution are mixed together as they enter the pressurizing pump.

8. The process of claim 1, wherein the metal containing solution is a metal salt solution.

9. The process of claim 1, wherein the salt is selected from the group consisting of nitrate, acetate, chloride, sulfate and bromide.

10. The process of claim 1, wherein the average particle size is less than about 10 nm.

11. The process of claim 1, wherein the average particle size is about 1 to 3 nm.

12. The process of claim 1, wherein the solid state material is crystalized.

13. The process of claim 1, wherein the metal containing solution and the precipitating agent solution are mixed together in a separate vessel.

14. A process for producing a calcined nanophase solid state material comprising (1) mixing together a metal containing solution and a second solution containing a precipitating agent to form a mixed solution, (2) pressurizing the mixed solution to a pressure of about 20,000 to 50,000 psig, (3) passing the pressurized mixed

solution into a fluidizing apparatus wherein high shear forces act on the mixed solution, creating nanophase solid state materials having nanosize particles having average sizes of from about 1 to 30 nm, (4) depressurizing the mixed solution so as to cause cavitation and calcination, and (5) separating the calcined nanophase solid material from the cavitated mixed solution.

15. The process of claim 14, wherein the metal containing solution and the precipitating agent containing solution are mixed prior to passage into the fluidizing apparatus.

16. The process of claim 14, wherein the mixed solution is recycled through the fluidizer apparatus.

17. The process of claim 16, wherein the precipitating agent solution is added to the mixed solution as it is recycled.

18. The process of claim 16, wherein the metal containing solution is added to the mixed solution as it is recycled.

19. The process of claim 14, wherein the metal containing solution and the precipitating agent solution are mixed together as they enter the pressurizing pump.

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[54] APPARATUS FOR PRODUCING
NANOSCALE CERAMIC POWDERS[75] Inventors: Joseph J. Helble, Andover, Mass.;
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R.I.[73] Assignee: Physical Sciences, Inc., Andover,
Mass.[*] Notice: The portion of the term of this patent
subsequent to Oct. 25, 2011 has been
disclaimed.

[21] Appl. No.: 61,069

[22] Filed: May 10, 1993

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 7,149, Jan. 21, 1993,
Pat. No. 5,358,695.[51] Int. Cl.⁶ C01B 13/20; C01B 13/18[52] U.S. Cl. 423/593; 501/1;
501/94; 423/594; 423/598; 423/599; 423/592;
423/600; 423/608; 423/618; 423/624; 423/632;
423/635; 423/610; 423/619; 423/625; 423/263[58] Field of Search 501/1, 94; 423/593,
423/594, 598, 600, 609, 618, 624, 632, 635, 592,
599, 610, 619, 625, 263

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Primary Examiner—Mark L. Bell

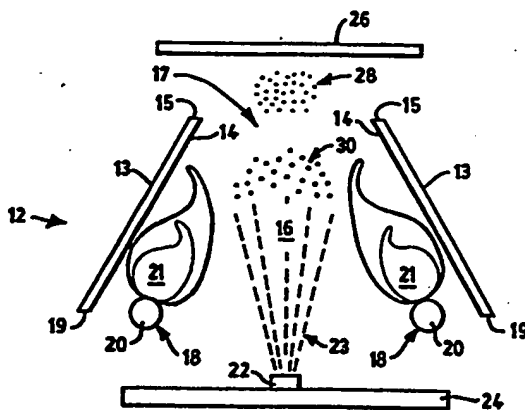
Assistant Examiner—C. M. Bonne

Attorney, Agent, or Firm—Testa, Hurwitz & Thibault

[57] ABSTRACT

An apparatus provides high temperature and short resi-
dence time conditions for the production of nanoscale
ceramic powders. The apparatus includes a confine-
ment structure having a multiple inclined surfaces for
confining flame located between the surfaces so as to
define a flame zone. A burner system employs one or
more burners to provide flame to the flame zone. Each
burner is located in the flame zone in close proximity to
at least one of the inclined surfaces. A delivery system
disposed adjacent the flame zone delivers an aerosol,
comprising an organic or carbonaceous carrier material
and a ceramic precursor, to the flame zone to expose the
aerosol to a temperature sufficient to induce combustion
of the carrier material and vaporization and nucleation,
or diffusion and oxidation, of the ceramic precursor to
form pure, crystalline, narrow size distribution, nano-
phase ceramic particles.

27 Claims, 3 Drawing Sheets



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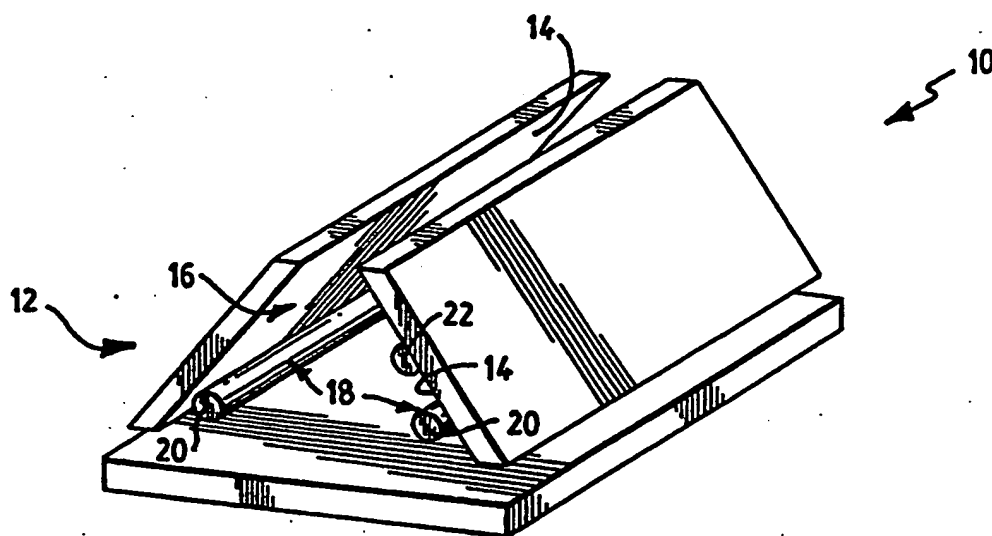


FIG. 1

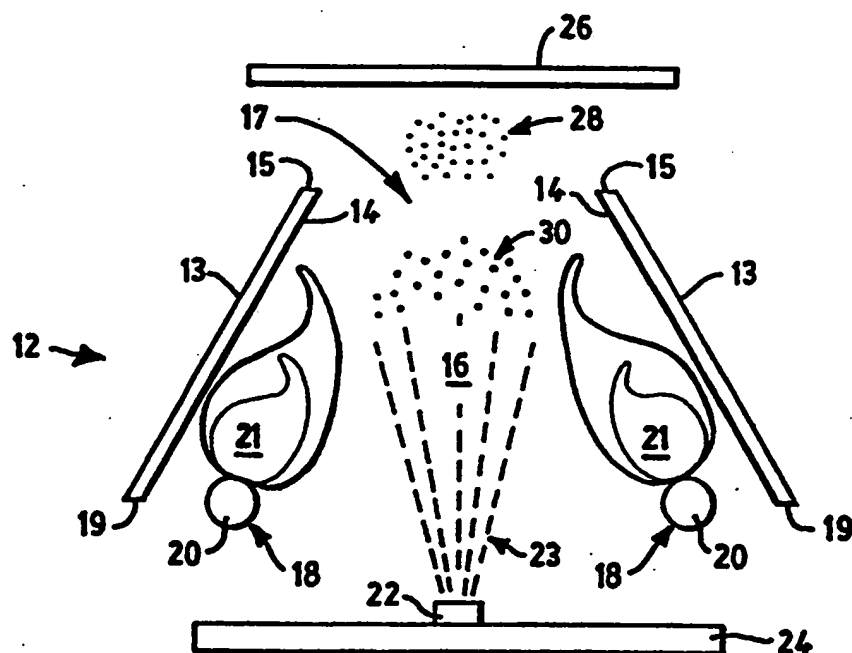


FIG. 2

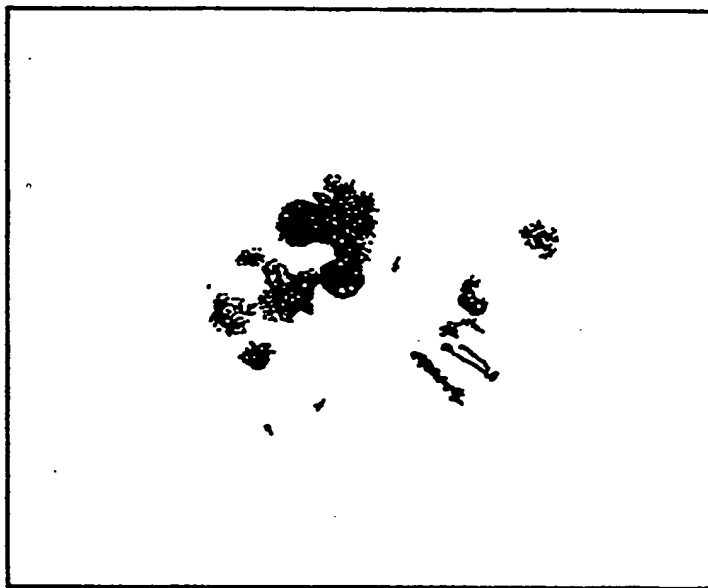


FIG. 3A

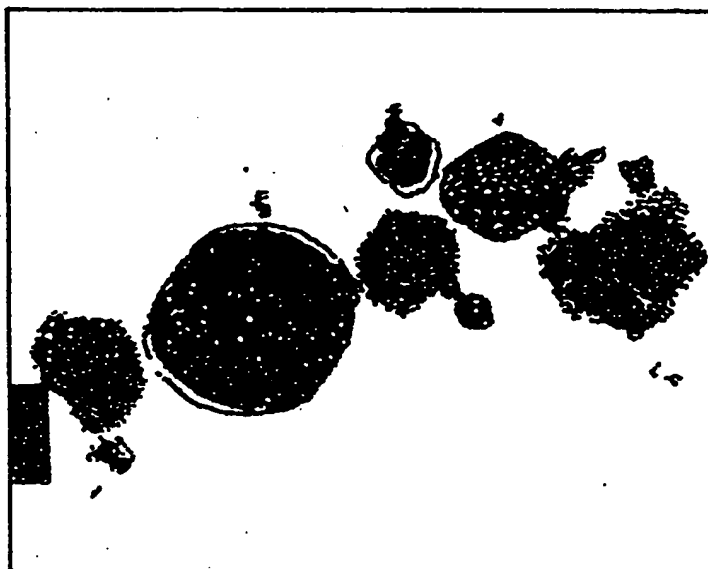


FIG. 3B

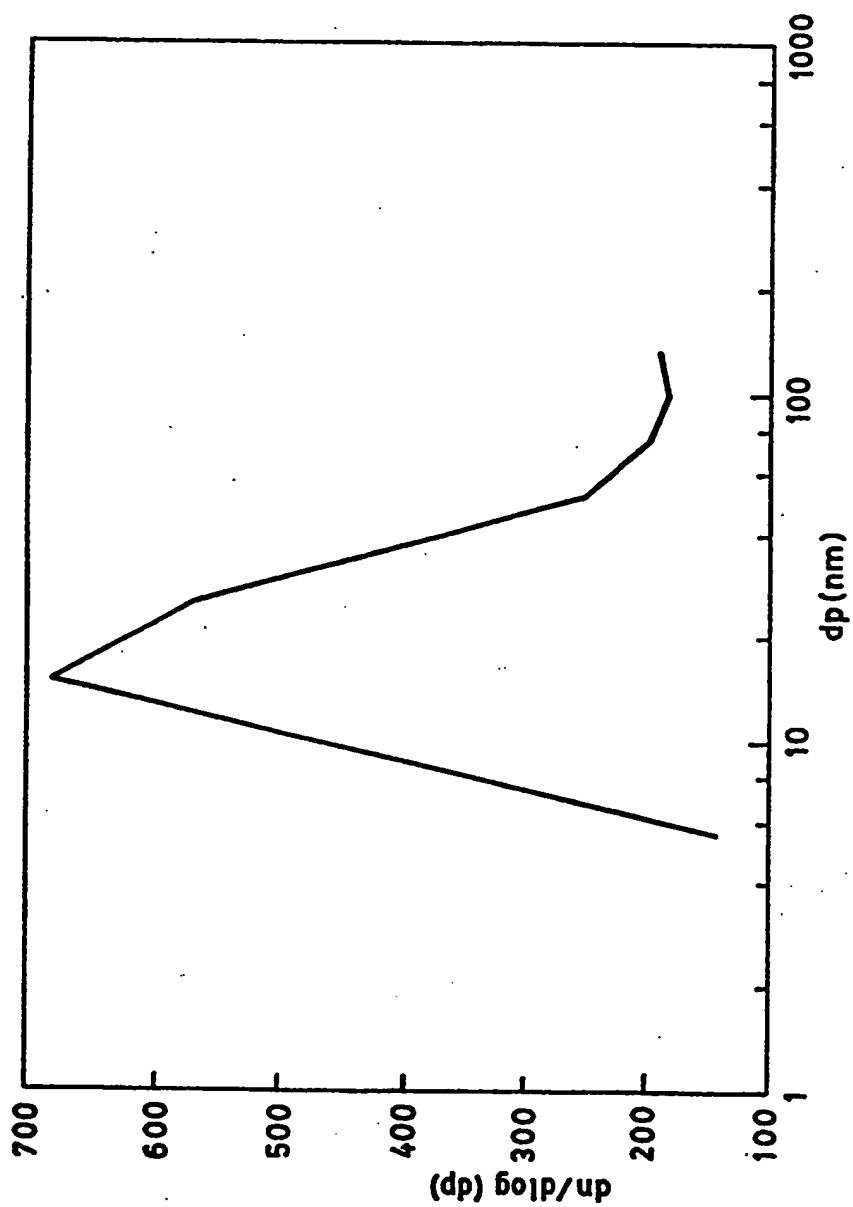


FIG. 4

APPARATUS FOR PRODUCING NANOSCALE CERAMIC POWDERS

GOVERNMENT INTEREST

The work described herein was supported in part by contracts with the Department of Energy and the Air Force Office of Scientific Research.

RELATED APPLICATION

This is a continuation-in-part of co-pending application U.S. Ser. No. 08/007,149, filed Jan. 21, 1993, now U.S. Pat. No. 5,358,695, the entire disclosure of which is hereby incorporated herein by reference.

BACKGROUND OF THE INVENTION

High-performance ceramic materials are essential for many engineering applications. Ultrafine ceramic powders are used to provide ceramic structures having the integrity, strength, and uniformity necessary to meet high performance requirements. To obtain many of the desirable properties associated with advanced ceramics, (e.g., toughness, high ductility, low sintering temperature and/or superplasticity) ceramic powders having nanometer scale crystalline grain structure, uniformity of crystalline phase, limited degree of particle aggregation, chemical purity, and narrow particle and grain size distributions are essential. Bowen, (1980) *Mater. Sci. Eng.*, 44:1; Andres et al, (1989) *J. Mater. Res.*, 4(3):704; Wakai and Nagano, (1991) *J. Mater. Sci.*, 26(1):241. Large scale exploration of the properties of these materials has been limited, however, by a lack of large quantities of inexpensive nanophase powder having the desired properties.

To address this need, researchers have been exploring many approaches to nanophase powder production. For example, spray drying or spray pyrolysis has been used to produce unagglomerated crystalline powders. In this process, precursor salts are dissolved in water which is sprayed into a high temperature environment. Ceramic particles form as a result of nucleation in the liquid phase, driven by evaporation of water. Although chemical purity is high, processing rates are limited by the need to maintain very low concentrations of precursor solute in the droplets to prevent formation of undesirable fragments and cenospheres. Kodas et al., (1988) *Appl. Phys. Lett.*, 52:1622; Zhang et al., (1990) *J. Am. Ceram. Soc.*, 73(1):61. Industrial flame processes such as SiCl_4 oxidation are inherently high rate processes. Such flame processes are best suited to single component systems such as TiO_2 or SiO_2 , and may produce sintered agglomerated powders having a large mean particle diameter due to the extended residence time at high temperature. Ulrich and Riehl, (1982) *J. Colloid Inter. Sci.*, 87:257. Further, ultrafine silica particles have been produced and deposited onto a fiber as part of a fiber optic waveguide manufacturing process. Morse, et al. *SPIE*, 1171-1207 (1989). None of the processes and devices described above meet the criteria for optimum production of nanophase ceramic powders, i.e., the high temperatures required for crystallinity and the short processing (residence) times required for minimal agglomeration.

SUMMARY OF THE INVENTION

The present invention features an apparatus useable in controlled vapor phase or droplet combustion processes for the production of submicron-sized ceramic

particles. The apparatus provides a high temperature flame environment and short residence times which are necessary for the controllable production of crystalline, single phase, unagglomerated submicron-sized ceramic particles.

In one embodiment, the apparatus comprises a confinement structure having a plurality of inclined surfaces. The confinement structure may, for example, include a pair of oppositely disposed inclined plates having planar inner surfaces. The inclined surfaces serve to confine flame located between the surfaces so as to define a flame zone. A burner system having one or more burners provides flame to the flame zone. It is noted herein that flame refers to one or more individual flames disposed within the flame zone. The burner system may, for example, include a ring burner or parallel, linear ribbon burners. Each burner is located in or near the flame zone in close proximity to at least one of the inclined surfaces. A delivery system is disposed adjacent the flame zone and delivers an aerosol, comprising an organic or carbonaceous carrier material and a ceramic precursor, to the flame zone to expose the aerosol to a temperature sufficient to induce combustion of the carrier material and vaporization and nucleation, or diffusion and oxidation, of the ceramic precursor to form pure, crystalline, uniform submicron-sized ceramic particles.

The delivery system may utilize a nozzle such as a piezoelectric nozzle. A horizontal base plate may also be provided; the nozzle protruding through the plate to deliver the aerosol to the flame zone for the production of the ceramic particles. The formed ceramic particles may be directed through an opening in the confinement structure defined by the distal edge of the inclined surfaces. A collection member may be disposed adjacent the distal edge of the confinement structure to collect the ceramic particles.

The present apparatus is structurally tailored to provide an environment which facilitates the production of unagglomerated, submicron-sized, crystalline ceramic particles. To that end, the confinement structure reduces heat loss so as to provide a uniformly high temperature in the flame zone. Further, the inclined surfaces of the confinement structure provide a degree of confinement for the reaction so that the resulting particles may be more easily collected. Also, the burner system minimizes the occurrence of cooler "edge regions" of the flame zone in which undesirable agglomeration of the particles may occur. Using the present apparatus, processing can be carried out in an environment including a uniform high temperature flame zone having substantially no edge regions, for short time periods to produce unagglomerated, submicron-sized, crystalline ceramic particles.

A method of controlled vapor phase or droplet phase combustion for producing submicron-sized ceramic oxide particles is also the subject of the present invention. In general, the process comprises forming an intimate mixture of an organic or carbonaceous carrier material and an organic or inorganic ceramic precursor, confining a flame generated by one or more burners within a high temperature flame zone defined by a plurality of inclined surfaces of a confinement structure, and delivering the mixture to the flame zone to expose the mixture to a flame zone temperature sufficient to cause the carrier material to oxidize and the ceramic precursor to form ultrafine, submicron-sized ceramic

particles. In this method, the heat resulting from the exothermic oxidation (i.e., combustion) of the carrier material causes the ceramic precursor to either vaporize and nucleate, or diffuse away from the burning carrier, thereby forming ceramic particles. The resulting particles are highly pure, crystalline and have a narrow particle size distribution. The particles are exposed to the heat of combustion for a very short time (e.g., a few milliseconds) such that agglomeration is minimized.

The first step of the process comprises combining a ceramic precursor material with organic or carbonaceous carriers. This step may be carried out in a number of ways, using any combustible organic or carbonaceous material as the carrier and any organic or inorganic metallic material that can form a ceramic under combustion conditions as the precursor. This step can be carried out, for example, by combining a ceramic precursor, such as a metal, metal salt, metal oxide or metal compound with a liquid organic matrix, such as a polymer or polymerizable monomer, and solidifying the matrix to form solid organic particles, or solid organic material which can be ground into particles, which contain the inorganic precursor. Alternatively, the ceramic precursor material can be colloidally dispersed in a solution of an organic carrier. In another embodiment, a ceramic precursor is dissolved or dispersed in an organic solvent, e.g., alcohol, or other suitable combustible solvent material. In yet another embodiment, a ceramic precursor is added to a solution of an organic material, such as a sugar or starch, and optionally combined with alcohol, and the resulting solution is sprayed, dried and ultimately combusted to form a powder. As demonstrated by these examples, any method can be used to form an intimate mixture of the combustible carrier and the ceramic precursor, as long as the mixture can be subsequently formed into an aerosol or fine spray of discrete droplets or particles for the combustion step.

The next step of the process involves delivering via a delivery system an aerosol spray of the discrete droplets or particles of the carrier/precursor to a flame, generated by a burner system, within a flame zone defined by the inclined surfaces of a confinement structure to expose the aerosol to a temperature in the flame zone sufficient to ignite the carrier material and cause combustion thereof. The burner system and the confinement structure may be the same as described previously in connection with the apparatus of the present invention. Combustion of the carrier portion of the aerosol creates myriad localized temperature gradients, and causes the ceramic precursor portion to either vaporized diffuse away from the burning carrier and nucleate; or to diffuse away by convective flow from the combusting carrier into the relatively cooler surrounding gas, forming the ceramic particles. For this step, a temperature of at least 1000K. and an atmosphere containing at least 20% (by volume) oxygen is preferred. The resulting particles can be collected and used in the desired application.

Ceramic particles which are less than 100 nm in diameter can be produced by the present apparatus and process. The particles produced are of narrow size distribution, pure, highly crystalline, and non-agglomerated. Ceramic particles produced according to the invention also sinter at lower temperatures than do conventional ceramic powders. The process can be used to produce large quantities of high-quality nanoscale ceramic particles for a variety of engineering applications.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing summary of the invention, and the various features thereof, as well as the invention itself may be more fully understood from the following detailed description when read together with the accompanying drawings.

FIG. 1 is perspective view of an apparatus for producing nanoscale ceramic particles in accordance with the principles of the invention.

FIG. 2 is detailed cross-sectional view of an apparatus for producing nanoscale ceramic particles.

FIGS. 3A and 3B are transmission electron microscope micrographs of particles of yttria-stabilized zirconia powder produced from zirconyl chloride precursors and dissolved in a sucrose/water solution with alcohol added.

FIG. 4 is a graph showing the size distribution of yttria-stabilized powder particles represented in FIGS. 3A and 3B.

DETAILED DESCRIPTION OF THE INVENTION

The development of advanced ceramic components requires large quantities of ceramic powders having nanometer scale grain structure and narrow grain size distribution. The grains or particles which comprise these powders must be chemically pure, crystalline, and narrowly agglomerated. The apparatus of the present invention provides a high temperature, short residence time environment for the production of nanometer scale ceramic oxide powders having all of these characteristics. The apparatus can be scaled up for producing such powders on an industrial scale.

A perspective view of an apparatus for producing nanoscale ceramic particles in accordance with the principles of the present invention is shown in FIG. 1. In general, the apparatus 10 comprises a confinement structure 12 having a plurality of inclined surfaces 14. The inclined surfaces 14 serve to confine flame located between the surfaces so as to define a flame zone 16. A burner system 18, having one or more burners, provides flame to the flame zone 16. Each burner 20 is located in or near the flame zone 16 in close proximity to at least one of the inclined surfaces 14. An aerosol delivery system 22 is disposed adjacent the flame zone 16 to deliver an aerosol, comprising an organic or carbonaceous carrier material and a ceramic precursor, to the flame zone for exposing the aerosol to a temperature sufficient to induce combustion (i.e. exothermic oxidation) of the carrier material and vaporization and nucleation, or diffusion and oxidation, of the ceramic precursor submicron-sized ceramic particles.

The present apparatus 10 is structurally tailored to provide an environment which facilitates the production of unagglomerated, nanoscale, crystalline ceramic particles. To that end, the confinement structure 12 preferably is formed of an insulating material to reduce heat loss so as to provide uniformly high temperatures in the flame zone 16. Further, the inclined surfaces 14 of the confinement structure provide an added degree of confinement for the reaction so that the resulting particles may be more easily collected. Also, the burner system 18 is configured to minimize the cooler "edge regions" of the flame zone in which undesirable agglomeration of particles may occur. The resulting environment, including a uniform high temperature flame

zone and substantially no edge regions, is well-suited for the production of high quality ceramic particles.

A detailed cross-sectional view of the present apparatus is shown in FIG. 2. The confinement structure 12, as shown, includes a pair of inclined plates 13. The plates 13 may be formed of smoked quartz or other insulating material and are arranged to provide a pair of oppositely disposed, inclined surfaces 14. These inclined, inner surfaces 14 serve to confine flame 21, which is provided during operation of the apparatus 10, located between the surfaces so as to define the flame zone 16. Further, the distal edges 15 of the respective, inclined surfaces define an opening 17 in the confinement structure 12.

Although a confinement structure including a pair of oppositely disposed, inclined surfaces is shown, it is noted that any confinement structure which includes a plurality of inclined surfaces arranged to define a flame zone can be employed without departing from the scope of the present invention. For example, a confinement structure including three inclined surfaces disposed in a pyramid-like arrangement can be used. Alternatively, a confinement structure including two pairs of oppositely disposed, inclined surfaces disposed in a box-like arrangement can also be used. The confinement structure also may be circular to form a substantially cone-shaped structure having a ring burner, or the like, disposed adjacent the base of the inclined surfaces.

The burner 18 system, as shown, includes a pair of parallel, linear burners 20 for providing flame 21 to the flame zone 16. Each burner 20 is disposed in or near the flame zone 16 in close proximity to the proximal edge 19 of one of the inclined surfaces 14. It is noted that the number and type of individual burners may be varied without departing from the scope of the invention. For example, each burner may be a ribbon burner such as those manufactured by Heathway Burner. Alternatively, each burner may be a row of linearly arranged, individual burner elements. Further, a ring burner or a circular arrangement of individual burner elements may be employed.

The delivery system 22 is disposed adjacent the flame zone and delivers an aerosol 23, comprising an organic or carbonaceous carrier material and a ceramic precursor, to the flame zone 16. The delivery system 22 may utilize a nozzle, such as a Sono-Tek extra length ultrasonic nozzle, or any other nozzle or atomizer-type delivery device. The nozzle may protrude through a central opening in a horizontal base plate 24 disposed opposite the opening 17 in the confinement structure 12. The aerosol 23 is directed by the nozzle to the flame zone 16 exposing the aerosol to a temperature sufficient to cause oxidation of the carrier material and the formation of ceramic particles 28. The particles 28 may be directed through the opening 17 and collected on a collection member 26 disposed adjacent the opening.

The present invention also includes a method for producing unagglomerated, crystalline ceramic particles in the range of 10 to 100 nm. To accomplish this, processing is preferably carried out in the present apparatus at high temperatures and for short periods of time, e.g., millisecond timescales. Processing for longer periods of time may lead to grain growth and particle agglomeration, while processing at lower temperatures may produce amorphous material requiring further heat treatment. Using the present apparatus, processing in its uniformly high temperature environment results in exothermic oxidation (i.e., combustion) of the organic or

carbonaceous carrier to generate steep localized temperature gradients. The organic or carbonaceous carrier burns completely away, and pure ceramic particles are formed. Growth of the ceramic particles can be precisely controlled using the apparatus and this process.

The steps in the present process are generally as follows: an organic or carbonaceous carrier material is combined with an organic or inorganic ceramic precursor to form an intimate mixture in which the ceramic precursor is closely associated with the carrier. For example, the carrier/precursor combination may be an organometallic compound or may be carbon carrier particles having the ceramic precursor adsorbed thereon. This mixture is atomized and delivered as an aerosol or fine spray to a flame zone defined by a plurality of inclined surfaces of a confinement structure as described above. The mixture is then exposed to a flame in the flame zone having a temperature sufficient to cause exothermic oxidation (combustion) of the carrier material. Combustion of the carrier generates intense, short-lived, local temperature gradients in the surrounding gas phase thereby inducing formation of ultrafine ceramic particles from the ceramic precursors. The very high temperature flame zone favors formation of crystalline structure in the ceramic particles and the short duration of combustion ensures that agglomeration does not occur. Thus, pure, crystalline, nanometer sized (e.g., about 10 nm to 100 nm) ceramic particles are formed.

The first step in the process comprises forming an intimate mixture of carrier material and a ceramic precursor material. The mixture preferably is formable into discrete droplets or particles. The carrier material can be any combustible organic or carbonaceous material, i.e., any carbon or carbon-hydrogen based material which reacts exothermically with oxygen. Exemplary carriers include carbon, carbon-based synthetic or natural polymers, organic solvents, such as alcohols, carbohydrates (such as sugars or starches) and other organic materials. Organometallic compounds may also be used. The ceramic precursor can be any material which forms a ceramic under oxidizing conditions. Exemplary ceramic precursors include metals, metal oxides, metal salts and other metal compounds. Mixtures of metals, metal salts, metal oxides, metal compounds or organometallic compounds can be used to produce heterogeneous powders. Metallic precursor compounds comprising two or more metals can be used to form multi-component powders. Inorganic materials (i.e., those lacking hydrocarbon components) can be used as precursors.

The mixture of carrier and precursor can be formed in a number of ways, including, for example, dissolving or dispersing the precursor into a solution or dispersion of the carrier and mixing together until an intimate mixture is obtained; or polymerizing organic monomers in the presence of precursors thereby forming polymer molecules containing the precursor. Liquid carrier/precursor mixtures or dispersions can be dried by spraying, air drying or other method which results in discrete droplets or particles. The preferred ratio of carrier to metal in the precursor is in the range of about 5:1 to about 100:1 on a weight basis.

In the next step, the carrier/precursor mixtures are delivered to a flame zone by a delivery system to be introduced into the high temperature environment of the flame zone. A flame generated by one or more burners of a burner system is confined with the flame zone,

which is defined by a plurality of inclined surfaces of a confinement structure. The burner system and confinement structure are preferably the same as described previously in connection with the present apparatus. The mixture is introduced as an aerosol or fine spray by the delivery system, such as by forcing it through an ultrasonic piezoelectric nozzle, by atomization or any other device. The temperature environment of the flame zone should be sufficiently high to cause the organic carrier to ignite and react exothermically (i.e., combustion). The high temperature environment preferably comprises a temperature at least 1000K. and an atmosphere of at least 20% (by volume) oxygen. The temperature range for applications of the present process can be from about 1200K. to about 3200K. However, higher or lower temperatures may be preferred for certain specific embodiments. The overall residence time in the high temperature environment typically is less than 5 seconds, more than 20 milliseconds, and preferably about 100 milliseconds. The residence time of the formed ceramic particles in the actual combustion zone (i.e., the burning carrier droplets) is believed to be less than about 50 μ s. Residence time in the cooler flame zone typically is about 100 milliseconds.

Following ignition of the carrier in the flame zone, a small combustion zone is created in the immediate vicinity of the carrier. The elevated temperatures associated with combustion cause the ceramic precursors associated with the organic material to either (a) decompose, vaporize, and diffuse away from the burning particles (referred to as the ceramic vapor pathway), or (b) diffuse away from the burning particles by convective flow (referred to as the colloidal pathway). Once these vapors or colloids encounter the surrounding oxygen-rich gases, the controlling physical phenomena differ slightly for each pathway, however, no differences in the product are noted. The ceramic vapor pathway and the colloidal pathway have been described in U.S. Ser. No. 08/007,149, which has been incorporated by reference, and are not described in detail herein.

In one embodiment of the present process, ceramic precursor compounds are dissolved in a combustible carrier solution such as an alcohol, and exposed to the flame process described above to form the nanoscale ceramic particles. Alcohols which are preferred include, for example, methanol, ethanol, propanol and butanol. In another embodiment, the ceramic precursor is mixed with an aqueous solution or dispersion of an organic or carbonaceous carrier material, such as a sugar, a starch, organic polymer or carbon, and processed as described above. For any of these embodiments, the solution, which includes a ceramic precursor and a combustible carrier, is fed through a delivery system to form an aerosol spray which is introduced into the flame zone of the present apparatus to produce nanoscale ceramic particles.

Commercially available combustible organometallic compounds were dissolved in alcohol, such as methanol or i-propanol, to provide a combustible precursor/carrier solution. These solutions were fed through a piezoelectric nozzle to the flame zone of the apparatus shown in FIG. 1 such that an aerosol was formed. The aerosol rapidly burned to yield nanoscale ceramic particles. Using this approach, oxides of aluminum, tantalum, titanium, silicon, and zirconium have been produced. A mixed yttrium-aluminum ceramic oxide/yttrium aluminum-garnet phase (YAG phase), has also been produced

by mixing yttrium and aluminum organometallic compounds in the appropriate ratios. In all of these situations, the particles had approximately the same size distribution and appearance. The resulting ceramic particles were typically spherical, touching only at the tangents of the spheres. Few examples of pronounced necking (i.e., the transition from single point particle contact to mass buildup between adjacent particles) were found. The high temperature combustion of the organometallic compound ensured that the organic residue was completely burned out, leaving only the desired nanoscale ceramic oxide particles as an end product.

In one specific example, zirconium propoxide (containing 23–28% n-propanol) and n-propanol were combined in a 2:1 mixture such that the resulting mixture was approximately 50% zirconium propoxide and 50% by weight n-propanol. While n-propanol was used, it is noted that other alcohols such as butanol could be used as the solvent. The ribbon burners of the apparatus were supplied with 7 slpm of methane and 17 slpm of oxygen. The resulting mixture was introduced into the flame zone in aerosol form. The alcohol carrier oxidized and burned away, thereby inducing formation of zirconium oxide particles. These particles had diameters in the 4–40 nm range with a mean diameter of about 38 nm. Other ceramic materials have been produced using this specific process, including oxides of aluminum, tantalum, titanium and yttria aluminum garnet (YAG phase).

Another embodiment of the process utilizes metallic compounds such as metal nitrates, hydroxides, and chlorides, associated with organic carriers. In this process, solutions, or dispersions of organic materials such as for example, sugars (e.g., sucrose or sorbitol), were dissolved in water, and the inorganic precursors were added. This mixture was then delivered as an aerosol to the flame zone of the present apparatus. Rapid combustion of the organic material in the aerosol spray, burning as individual droplets rather than as a homogeneous vapor, resulted in the production of nanophase, unagglomerated, crystalline ceramic oxide powders. In a separate process, the precursor/carrier was mixed with alcohol, (e.g., methanol) either alone or in combination with water, as the solvent to increase flame temperatures. In each process, the sucrose or sorbitol droplets remained intact in the initial stages of the flame, thus ensuring that single particle (droplet) combustion occurred. It is noted that the use of a volatile organic solvent (e.g., alcohol) results in vapor phase combustion. This embodiment relies on (slightly viscous) droplet combustion to ensure that the droplets remain intact. This is distinguishable from vapor phase combustion, as it limits agglomeration by keeping the reacting particles separated. Further, droplet combustion eliminates the need for expensive combustible organometallic compounds. Instead, inexpensive precursor compounds (e.g., acetates, nitrates, chlorides, etc.) can be dissolved or dispersed in a combustible organic solvent. Colloidal precursors, e.g. colloidal zirconium plus yttrium salts, may be used to make the same product if a process utilizing organic spray droplet combustion is used.

In one specific example, zirconyl chloride (15.9 g) was added to water (78 g). Yttrium nitrate (3.43 g) was subsequently added, and the solution was stirred to dissolve the compounds. Next, sucrose (150 g) was added, and the solution was stirred to dissolve the sucrose. It is noted that other sugars, such as fructose and sorbitol, have been used in other examples. Methanol

(230 g) was added, and the solution was once again stirred. Using a pump, the solution was forced into a nozzle to produce a spray. The spray was introduced into the flame zone of the present apparatus, resulting in zirconium oxide particles having a mean diameter of 37 nm.

In another specific example, a mixture including zirconium salts and yttrium salts was introduced as an aerosol into the flame zone of the present apparatus. Yttria-stabilized zirconia with particles having a 40 nm mean size was the end product (FIG. 3A and 3B). The particle size distribution is shown in FIG. 4. X-ray diffraction revealed that this was a single-phase crystalline material. Sintering tests subsequently conducted with uniaxially-pressed pellets of this powder demonstrated extensive densification at 1000° C. at least 300° C. lower than the sintering temperatures reported in the literature for larger-grained commercial zirconia powders.

Nanoscale ceramic particles produced according to the present process can be used to make high performance ceramic materials for microelectronics, biotechnology and engineering applications. Ceramic materials typically are made by molding the ceramic powders and sintering the molded article at high temperatures to densify the ceramic. Ceramic powders having a small, uniform particle size permit closer packing, thus, the sintered body has smaller residual pores and fewer voids. Nonuniform particle size, the presence of agglomerated particles and impurities in the powder make sintering more difficult and require higher sintering temperatures resulting in formation of internal flaws and voids which weaken the final ceramic structure. The present pure, crystalline unagglomerated ceramic powder sinters at a lower temperature, and the small particle size and uniform particle size distribution allows it to compact well and minimizes the occurrence of voids. Thus, high integrity, high performance ceramics having excellent structural characteristics can be produced.

EQUIVALENTS

From the foregoing description, one skilled in the art can ascertain the essential characteristics of this invention and without departing from the spirit and scope thereof, can make various modifications of the invention which are equivalent. Such equivalents are intended to be encompassed by the following claims.

We claim:

1. A process for producing submicron-sized ceramic particles comprising the steps of: confining a flame generated by one or more burners to a flame zone between a plurality of inclined surfaces;

forming an intimate mixture comprising a ceramic precursor and an organic or carbonaceous carrier material; and

delivering the mixture to the flame zone to expose the mixture to the flame to induce (i) combustion of the carrier material, and (ii) vaporization and oxidation of the ceramic precursor and nucleation of the ceramic particles, or diffusion of the ceramic precursor away from the carrier material and oxidation, thereby forming substantially non-agglomerated ceramic particles.

2. The process of claim 1 wherein the ceramic particles are less than 100 nm in diameter.

3. The process of claim 1 wherein the ceramic particles are crystalline.

4. The process of claim 1 wherein the ceramic precursor comprises a metal, metal salt, metal oxide, or organometallic compound.

5. The process of claim 4 wherein the metal is selected from the group consisting of titanium, iron, aluminum, zirconium, magnesium, barium, lead and yttrium.

6. The process of claim 4 wherein the ceramic precursor comprises a mixture of two or more metals, metal salts, metal oxides, or organometallic compounds.

7. The process of claim 4 wherein the ceramic precursor is a metal compound comprising two or more metals.

8. The process of claim 1 wherein the carrier material is a carbohydrate.

9. The process of claim 8 wherein the carbohydrate is sucrose, fructose or sorbitol.

10. The process of claim 1 wherein the carrier material is an alcohol.

11. The process of claim 1 wherein the carrier material is carbon.

12. The process of claim 1 wherein the combustion step is carried out a temperature above about 1000 K.

13. A process for producing submicron-sized ceramic particles comprising the steps of:

confining a flame generated by one or more burners to a flame zone between a plurality of inclined surfaces;

combining a ceramic precursor with an organic or carbonaceous carrier material forming a combination in which the precursor is associated with the carrier material;

atomizing the combination thereby forming an aerosol;

delivering the aerosol via a delivery system to the flame zone to expose the aerosol to a temperature in the flame zone sufficient to cause (i) combustion of the carrier material, and (ii) vaporization and oxidation of the ceramic precursor and nucleation of the ceramic particles, or diffusion of the ceramic precursor away from the carrier material and oxidation, thereby forming substantially non-agglomerated ceramic particles.

14. The process of claim 13 wherein the ceramic particles are less than 100 nm in diameter.

15. The process of claim 13 wherein the ceramic particles are crystalline.

16. The process of claim 13 wherein the ceramic precursor is a metal, metal salt, metal oxide or organometallic compound.

17. The process of claim 16 wherein the metal is selected from the group consisting of titanium, iron, aluminum, zirconium, magnesium, barium, lead and yttrium.

18. The process of claim 16 wherein the ceramic precursor comprises a mixture of two or more metals, metal salts, metal oxides or organometallic compounds.

19. The process of claim 16 wherein the ceramic precursor is a metal compound comprising two or more metals.

20. The process of claim 13 wherein the carrier material is a carbohydrate.

21. The process of claim 20 wherein the carbohydrate is sucrose, fructose or sorbitol.

22. The process of claim 13 wherein the carrier material is an alcohol.

23. The process of claim 13 wherein the carrier material is carbon.

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24. The process of claim 13 wherein the combustion step is carried out a temperature above about 1000 K.

25. A process for producing submicron-sized ceramic particles comprising the steps of:

forming an intimate mixture comprising a ceramic precursor and an organic or carbonaceous carrier material; and

delivering the mixture to a flame that is confined within a plurality of inclined surfaces, thereby exposing the mixture to a high temperature flame zone having substantially no edge regions to form substantially non-agglomerated ceramic particles.

26. A process for producing submicron-sized ceramic particles comprising the steps of:

forming an intimate mixture comprising a ceramic precursor and an organic or carbonaceous carrier material; and

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delivering the mixture to a flame confined by a plurality of inclined surfaces to expose the mixture to a flame zone having uniformly high temperature and substantially no edge regions, thereby causing (i) combustion of the carrier material, (ii) vaporization and oxidation of the ceramic precursor and nucleation of the ceramic particles, or diffusion of the ceramic precursor away from the carrier material and oxidation, and (iii) formation of substantially non-agglomerated ceramic particles.

27. A process for producing submicron-sized ceramic particles comprising the steps of:

forming an intimate mixture comprising a ceramic precursor and an organic or carbonaceous carrier material; and

exposing the mixture to a high temperature flame zone having substantially no edge regions to form substantially non-agglomerated ceramic particles.

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US005635154A

United States Patent [19]

Arai et al.

[11] Patent Number: **5,635,154**[45] Date of Patent: **Jun. 3, 1997**[54] **PROCESS FOR PRODUCING FINE METAL OXIDE PARTICLES**[75] Inventors: **Kunio Arai; Tadafumi Ajiri**, both of Sendai, Japan[73] Assignee: **Nissan Chemical Industries Ltd.**, Tokyo, Japan[21] Appl. No.: **448,025**[22] Filed: **May 23, 1995****Related U.S. Application Data**

[62] Division of Ser. No. 714,225, Jun. 12, 1991, Pat. No. 5,480,630.

[30] **Foreign Application Priority Data**

Jun. 15, 1990 [JP] Jap. a. _____ 2-157317

[51] Int. Cl.⁶ _____ C01B 13/14; C01F 11/00; C01G 49/02; C01G 3/02

[52] U.S. Cl. _____ 423/592; 423/593; 423/263; 423/325; 423/632; 423/633; 423/604; 423/636; 423/622; 423/618; 423/608; 423/617; 423/607; 423/605

[58] Field of Search _____ 423/632, 141, 423/93, DIG. 11, 633, 634, 592, 593, 604, 636, 622, 263, 325, 618, 608, 617, 607, 605, 159

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Disclosed herein is a process for producing fine metal oxide particles comprising the step of heat-treating an aqueous solution of a metal salt at a temperature of not lower than 200° C. under a pressure of not less than 160 kg/cm² for 1 second to 1 hour so as to bring into the decomposition reaction of said metal salt.

4 Claims, 4 Drawing Sheets



FIG. 1

500 nm



FIG. 2

500 nm



FIG. 3

100 nm

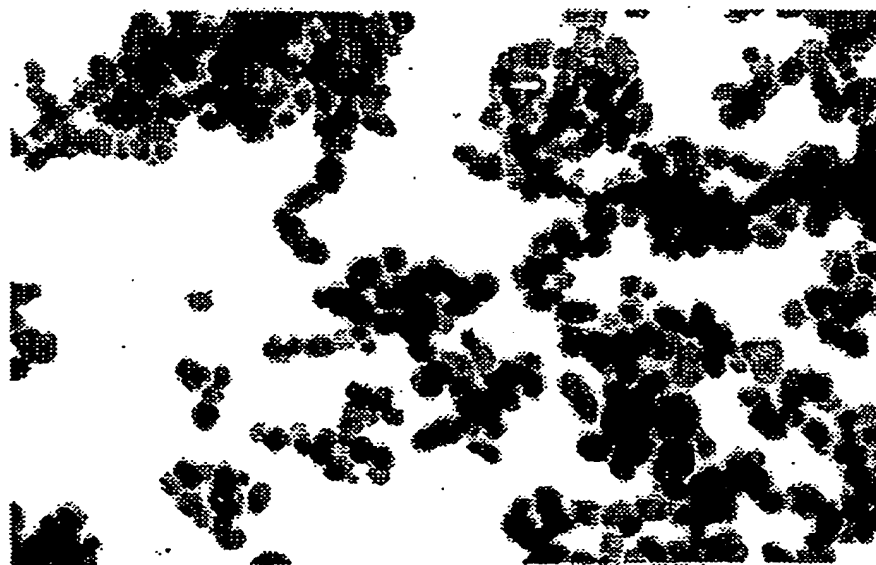
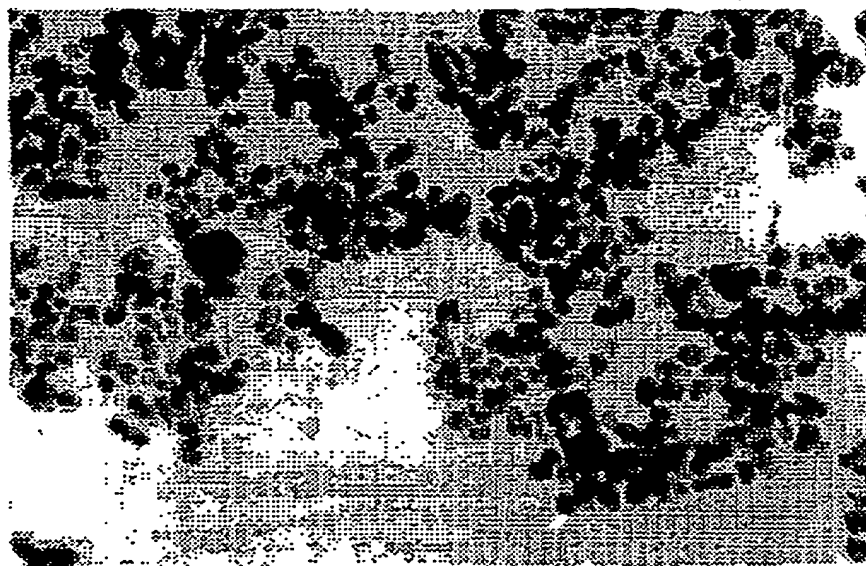


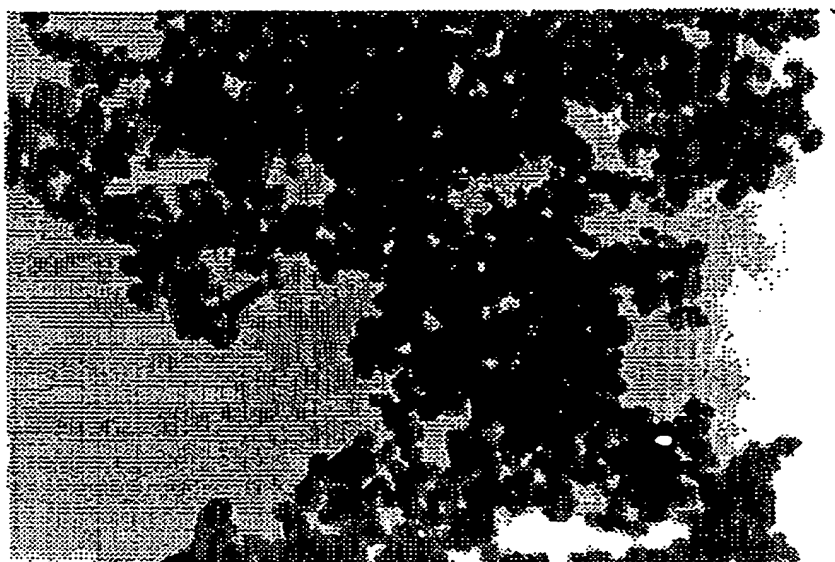
FIG. 4

100 nm



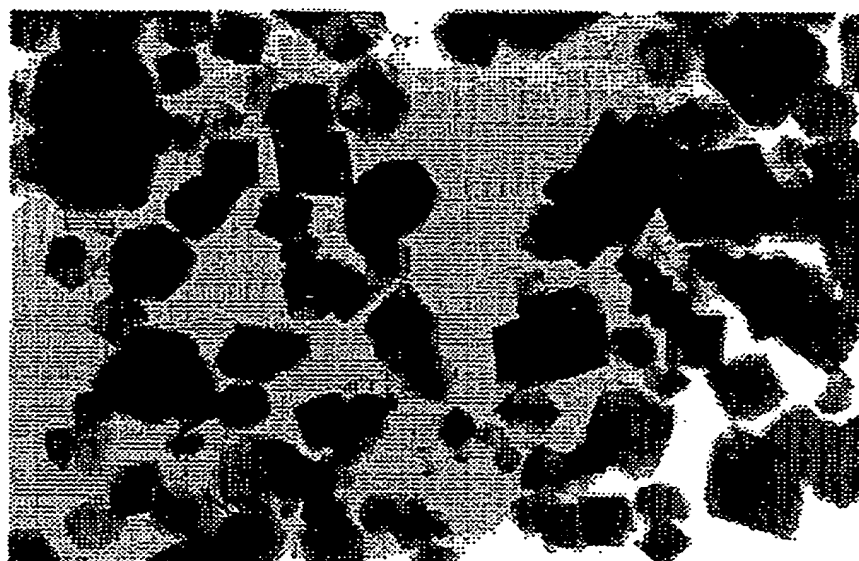
100 nm

FIG. 5



100 nm

FIG. 6



100 nm

FIG. 7

PROCESS FOR PRODUCING FINE METAL OXIDE PARTICLES

This is a division of application Ser. No 07/714,225 filed on Jun. 12, 1991, now U.S. Pat. No. 5,480,630.

BACKGROUND OF THE INVENTION

The present invention relates to a process for producing fine metal oxide particles and, more particularly, to a process for producing fine metal oxide particles by heat-treating an aqueous solution of a metal salt under the subcritical to supercritical conditions for water.

The fine metal oxide particles are used in various fields, for example, as a material of ceramics, electronic devices, catalysts, cosmetics and coatings, reinforcing materials and fillers for modifiers, and various methods of producing the fine metal oxide particles are conventionally known.

The fine metal oxide particles used in the above fields are required to have a narrow particle size distribution width and the uniform shape, to be free from a dendrite or a crystal twinning, and to have few secondary agglomerates. The fine metal oxide particles are sometimes required to be uniformly agglomerated or amorphous to a great extent.

Such fine metal oxide particles are conventionally produced by coprecipitation method, heat hydrolysis method or autoclaving method. In the coprecipitation method, the particle size is greatly influenced by the temperature, concentration, charging ratio, charging rate, method of supplying the raw materials, and stirring, so that the particle diameter is not always uniform, resulting in a wide particle size distribution width. To prevent this, various means are taken such as the addition of various additives and the aging of the fine particles after the completion of the reaction.

In the heat hydrolysis method and the autoclaving method, an autoclave is used and a comparatively long reaction time or aging time such as 30 minutes to 48 hours is necessary.

That is, no process for producing the fine metal oxide particles with high productive efficiency has not been established.

As a result of various investigations by the present inventors, it has been found that by heat-treating an aqueous solution of a metal salt under the subcritical to supercritical conditions for water fine metal oxide particles having excellent characteristics such as narrow particle size distribution width and uniform particle shape can be obtained in a short time. The present invention has been achieved on the basis of this finding.

SUMMARY OF THE INVENTION

In an aspect of the present invention, there is provided a process for producing fine metal oxide particles comprising the step of heat-treating an aqueous solution of a metal salt under a pressure of not less than 160 kg/cm² and at a temperature of not lower than 200° C. to achieve a decomposition reaction of the metal salt.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an electron micrograph of the particle structure of the boehmite obtained in Example 1;

FIG. 2 is an electron micrograph of the particle structure of the boehmite obtained in Example 3;

FIG. 3 is an electron micrograph of the particle structure of the boehmite obtained in Example 5;

FIG. 4 is an electron micrograph of the particle structure of the α -Fe₂O₃ obtained in Example 7;

FIG. 5 is an electron micrograph of the particle structure of the γ -Fe₂O₃ obtained in Example 8;

FIG. 6 is an electron micrograph of the particle structure of the Fe₃O₄ obtained in Example 10; and

FIG. 7 is an electron micrograph of the particle structure of the Fe₃O₄ obtained in Example 11.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The metal salt used in the present invention is not specified so long as it is water-soluble. For example, the metal salts of the metals of IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIB and VIIB groups and transition metals are usable. More concretely, inorganic acid salts such as nitrates, chlorides, sulfates, oxyhydrochlorides, phosphates, borates, sulfites, fluorides and oxyacid salts of Cu, Ba, Ca, Zn, Al, Y, Si, Sn, Zr, Ti, Sb, V, Cr, Mn, Fe, Co and Ni, and organic acid salts such as formates, acetates, citrates, oxalates and lactates of Cu, Ba, Ca, Zn, Al, Y, Si, Sn, Zr, Ti, Sb, V, Cr, Mn, Fe, Co and Ni may be exemplified. These metal salts may be used in the form of a mixture. The complexes of these metals are also usable. If the corrosion of the material of the apparatus or the like is taken into consideration, nitrates are preferable.

The concentration of the metal salt in the aqueous solution does not specified so long as it is dissolved, but the preferred metal salt concentration is 0.0001 to 1 mol/l.

A batch-type reaction process or a semi-batch-type reaction process is usable, but a continuous reaction process which charges the stock solution in a tubular

is preferable. The reaction temperature and the reaction pressure is not less than 200° C. and not less than 160 kg/cm², respectively, which are the subcritical or supercritical conditions for water. The preferable reaction temperature is 300 to 500° C. and the preferable reaction pressure is 250 to 500 kg/cm². The reaction is especially preferably carried out under the supercritical conditions for water.

The reaction time in the reactor is different depending upon the reaction conditions, but ordinarily 1 second to 1 hour, preferably 1 to 10 minutes.

The reaction product is collected by cooling it before the reaction pressure is reduced and (i) causing it to flow out to a constant-pressure system at a constant speed through a reducing valve or (ii) reducing directly the reaction pressure to the ordinary pressure.

In the present invention, an alkali and/or acidic aqueous solution may be added to an aqueous solution of a metal salt. As examples of the alkali may be exemplified ammonia, sodium hydroxide and potassium hydroxide, and as examples of the acid may be exemplified inorganic acids such as sulfuric acid, nitric acid, hydrochloric acid, carbonic acid and phosphoric acid, and organic acids such as formic acid, acetic acid, citric acid, oxalic acid and lactic acid.

In the present invention, a reducing gas such as hydrogen or an acidic gas such as oxygen may be introduced into an aqueous solution of a metal salt.

In order to separate the target fine metal oxide particles from the thus-obtained reaction product, a known method may be adopted. For example, the separation may be carried out by filtration, centrifugal separation, spray drying or ultrafiltration. It is also possible to directly obtain the dried fine metal oxide particles by reducing directly the reaction pressure to the ordinary pressure without cooling the reaction product.

Under the subcritical to supercritical conditions for water, the dissociation of water is enhanced to a great extent, and water acts on the aqueous solution of the metal salt as a stronger acid, thereby greatly facilitating the progress of the hydrolysis reaction or the metathetical reaction of the metal salt. In addition, since the physical properties such as the ionic product, dielectric constant, diffusion rate and thermal conductivity of a fluid greatly vary under the subcritical to supercritical conditions, it is easy to control the shape and the size of the fine metal oxide particles by controlling the reaction route and the reaction rate. It is possible to make the heat-transfer coefficient larger under the subcritical to supercritical conditions than in a gaseous phase and the diffusion coefficient much larger than in a liquid phase. It is, therefore, possible to make the reaction conditions in the reactor uniform in a wide range including a micro size at a molecular level, thereby suppressing the increase in the particle diameter distribution width and the scatter in the particle shape which are derived from the scatter in temperature gradient, pressure gradient or concentration.

As described above, according to the present invention, it is possible to finish the reaction in a short time and to further easily obtain the fine metal oxide particles having uniform particle diameter and shape by varying the reaction conditions such as the concentration of the raw material, addition of an alkali or an acid, introduction of a reducing gas or an acidic gas, the reaction temperature and the reaction pressure.

The shape of the fine particles of a metal oxide obtained by the process of the present invention is spindle-like, acicular, scale-like, hexagonal plate-like, square plate, ellipsoid, sphere, octahedron, or the like. The shape can be selected by varying the reaction conditions. Namely, the fine metal oxide particles obtained having a narrow particle size distribution width [for example, particle size distribution width = $(0.7-1.3) \times$ average particle size] in the particle size range of a major axial diameter of 100 to 2000 nm and a minor axial diameter of 50 to 1000 nm in the case of spindle-shaped particles; a major axial diameter of 100 to 1000 nm and a minor axial diameter of 20 to 200 nm in the case of acicular particles; a plane diameter of 100 to 2000 nm in the case of scale-like particles; a plate diameter of 100 to 1000 nm in the case of hexagonal plate-like particles; a side 50 to 1000 nm long in the case of square plate-like particles; a major axial diameter of 30 to 300 nm and a minor axial diameter of 20 to 200 nm in the case of ellipsoidal particles; a particle diameter of 20 to 500 nm in the case of spherical particles; and a particle diameter of 20 to 1000 nm in the case of octahedral particles.

Accordingly, the fine metal oxide particles produced by the process of the present invention are useful as a raw material of ceramics, electronic devices, catalysts, cosmetics and coatings, reinforcing materials and fillers for modifiers.

EXAMPLES

The present invention will be explained in more detail hereinafter with reference to the following examples.

In the examples, the reacting apparatuses A and B which will be described in the following were used.

(Reaction apparatus A)

The suction portion of a pressure pump is introduced into an aqueous solution of the raw material through a pipe, and the discharging portion of the pump is connected to a stainless steel pipe 3.18 mm in outer diameter and 1.85 mm in inner diameter which is coiled to a length of 12 m. This reactor is placed in a heating furnace and a cooling portion is provided at the exit of the heating portion. A reducing valve is provided so that the reaction product is collected to a collector at a constant pressure.

(Reaction apparatus B)

An apparatus similar to the reaction apparatus A except that the reactor in apparatus A is replaced by a stainless pipe having an outer diameter of 9.53 mm, an inner diameter of 6.23 mm, and a length of 400 mm.

Example 1

An aqueous solution of aluminum nitrate having a concentration of 0.01 mol/l was charged into the reaction apparatus A and brought into a decomposition reaction at a flow rate of 4 ml/min at a temperature of 350° C. under a pressure of 300 kg/cm². The reaction product obtained was a cloudy aqueous solution. From the X-ray analysis of the powder obtained by filtering and drying the reaction product, it was observed that 100% boehmite (AlOOH) had been produced. The uniformly spindle-shaped particles having a particle diameter of 1500×700 nm were observed in an electron micrograph, as shown in FIG. 1.

Examples 2 to 12

Aqueous solution of metal salts shown in Table 1 were brought into a decomposition reaction by using the reaction apparatus A or B under the conditions shown in Table 1 in the same way as in Example 1. The reaction products were analyzed with X-rays and the shapes of the particles were observed in electron micrographs. The typical examples of the electron micrograph are shown in FIGS. 2 to 7.

As shown in Table 1, boehmite particles varying in shape and size were obtained from aluminum nitrate, as shown in Table 1.

In the case of using an iron salt, various substances were produced under the influence of anions and cations. The lower the concentration of the raw material, the finer were the particles obtained.

TABLE 1

Example No.	Reaction Apparatus	Reaction conditions			Pressure (kg/cm ²)	Flow rate (ml/min)	Reaction products		
		Metal salt	Concentration (mol/l)	Temperature (°C.)			X-ray analysis	Particle shape	Particle size (nm)
1	A	Aluminum nitrate	0.01	350	300	4	Boehmite	Spindle-like	1500 × 700
2	A	Aluminum	0.053	400	300	4	-	Acicular	700 × 100

TABLE 1-continued

Example No.	Reaction Apparatus	Reaction conditions				Flow rate (ml/min)	Reaction products		
		Metal salt	Concentration (mol/l)	Temperature (°C.)	Pressure (kg/cm ²)		X-ray analysis	Particle shape	Particle size (nm)
3	A	Aluminum nitrate	0.01	300	400	4	"	Scale-like	200
4	A	Aluminum nitrate	0.01	400	400	4	"	Hexagonal plate-like	300
5	A	Aluminum nitrate	0.002	400	350	4	"	Square plate-like	200
6	A	Aluminum nitrate	0.0004	400	350	4	"	Square plate-like	100
7	B	Fe(NO ₃) ₃	0.1	400	350	4	α -Fe ₂ O ₃	Ellipsoidal	50-100
8	B	"	0.02	400	350	4	α -Fe ₂ O ₃	"	30-60
9	A	Fe ₂ (SO ₄) ₃	0.01	400	400	4	α -Fe ₂ O ₃ + Fe ₃ O ₄	Spherical	20
10	B	Ferric ammonium citrate	0.02	400	350	6	Fe ₃ O ₄	Ellipsoidal	20-50
11	B	Cobalt nitrate	0.02	400	350	5	Co ₃ O ₄	Octahedral	40-250
12	B	Nickel nitrate	0.02	400	350	6	NiO	Acicular	100 x 400

What is claimed is:

1. A process for producing fine metal oxide particles having a particle size of 20 to 2,000 nm comprising the steps of heat-treating an aqueous solution of a water-soluble metal salt at a temperature of not lower than 200° C. at a pressure of 250 to 500 kg/cm² for 1 second to 10 minutes to achieve a decomposition reaction of said metal salt to form said metal oxide, wherein said aqueous solution of said metal salt is continuously supplied in a tubular reactor in such a manner as to remain in a reaction zone of the tubular reactor at a temperature of not lower than 200° C. and a pressure of 250 to 500 kg/cm² for 1 second to 10 minutes, and separating said fine metal oxide particles, and wherein said metal is selected from the group consisting of copper, barium,

calcium, zinc, yttrium, silicon, tin, zirconium, titanium, antimony, vanadium, chromium, manganese, iron, cobalt and nickel.

2. A process according to claim 1, wherein an alkali or acidic aqueous solution is added to said aqueous solution of said metal salt.

3. A process according to claim 1, wherein a reducing gas comprising hydrogen or an acidic gas containing oxygen is introduced into said aqueous solution of said metal salt.

4. A process according to claim 1 wherein the temperature is from 300° to 500°.

* * * * *

United States Patent [19]

Ota et al.

[11] Patent Number: 4,705,762

[45] Date of Patent: Nov. 10, 1987

[54] PROCESS FOR PRODUCING ULTRA-FINE CERAMIC PARTICLES

[75] Inventors: Kazuhide Ota, Okazaki; Susumu Abe, Toyota, both of Japan

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[21] Appl. No.: 699,909

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[58] Field of Search 423/DIG. 10, 335, 439, 423/625, 636, 610, 608, 633, 412, 409, 411; 501/1, 87, 96, 108, 127, 133, 134, 153, 154

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[57] ABSTRACT

A process for producing ultra-fine ceramic particles with the particle size of less than 1000 Å, which comprises the steps of forming powdered dust cloud of metal powder such as Si constituting a portion of aimed ceramic particles in a reaction gas containing the other portion of said aimed ceramic particles, igniting said powdered dust cloud to cause explosive burning and synthesizing said aimed ceramic particles and gathering said resulting ceramic particles. By the process, ceramic particles such as Al₂O₃, MgO, SiO₂, TiO₂, TiN having particle size of 10–100 nm can be produced.

25 Claims, 3 Drawing Figures

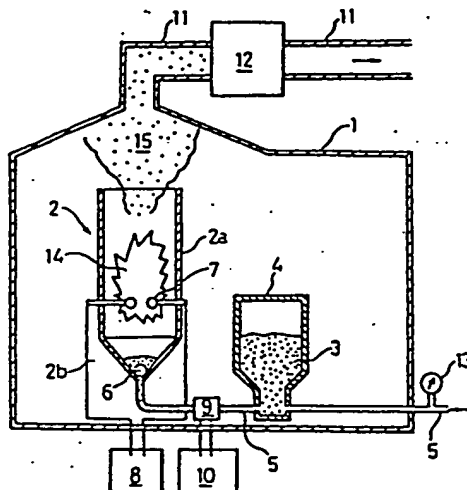


FIG. 1

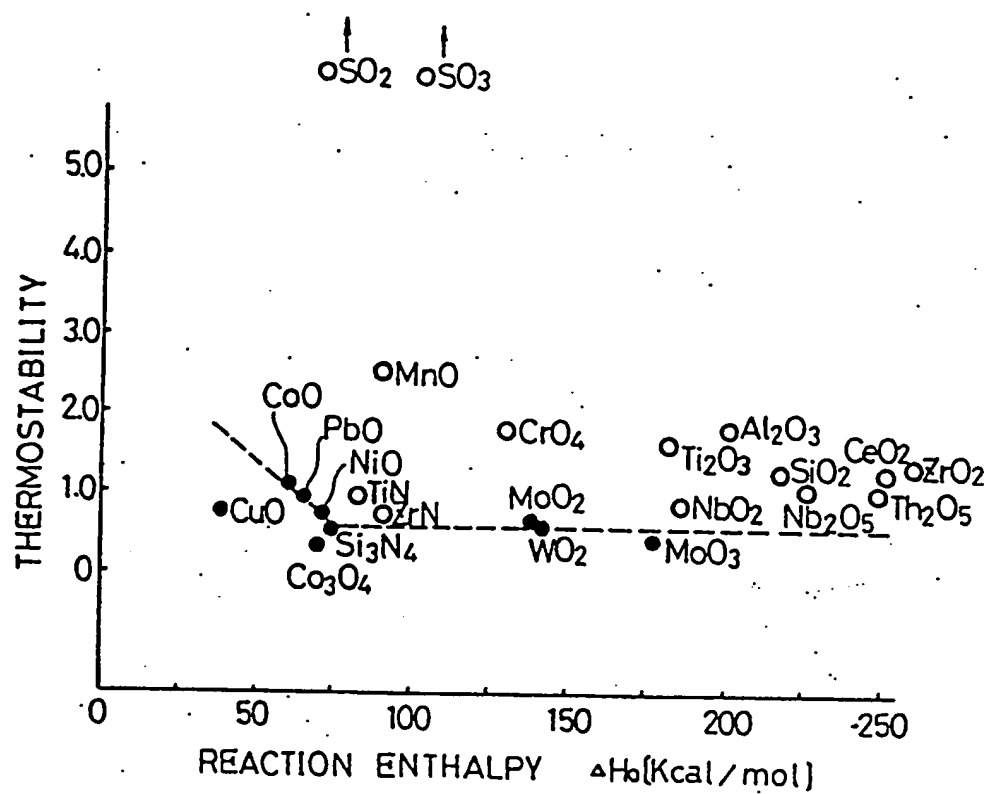


FIG. 2

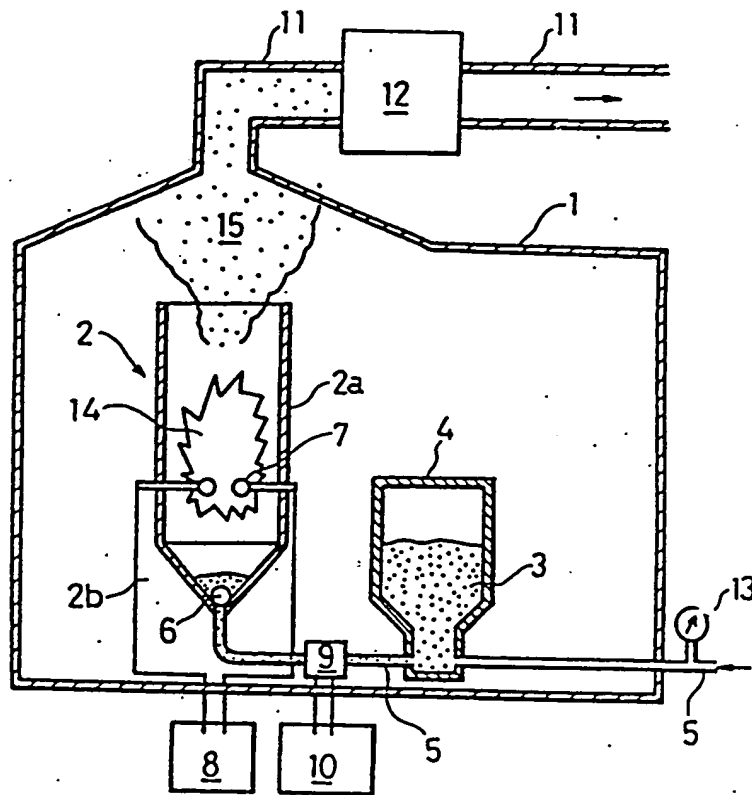
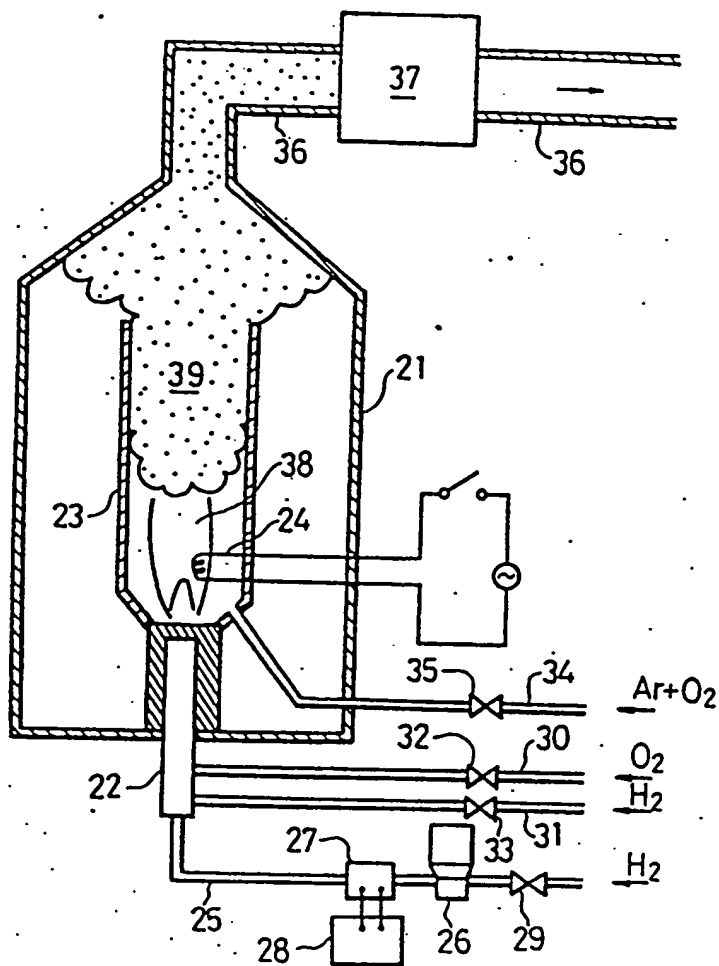


FIG. 3



PROCESS FOR PRODUCING ULTRA-FINE CERAMIC PARTICLES

BACKGROUND OF THE INVENTION

1. Field of the Invention

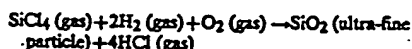
This invention concerns a process for producing ultra-fine ceramic particles utilizing powdered dust explosion.

2. Description of the Prior Art

Ultra-fine ceramic particles with the particle size of less than 1000 Å are of a great surface energy and, accordingly, have an advantage of easy sintering at low temperature and increased catalytic activity, and the mass production of such ultra-fine ceramic particles at a reduced cost has been demanded.

The production process for such ultra-fine ceramic particles are largely classified into the physical process and the chemical process.

The method of producing ultra-fine ceramic particles by using the chemical process includes a vapor phase chemical reaction process utilizing the reaction often employed in chemical vapor deposition process (CVD), for example, as shown in "Production of finely powdered material and technic for the surface improvement" in "Chemical Technology", p 525-529, published in October 1982. As the heat source for the gas phase chemical reaction process, arc, plasma, chemical flame or the like can be used. The chemical flame process includes examples of synthesizing ultra-fine oxide particles from volatilizing metal halides by using H_2-O_2 flame or $C_2H_2-O_2$ flame. For instance, ultra high purity silica for use in the matrix of optical fibers is synthesized by the reaction shown by the following equation:



In the above-mentioned reaction, silicon tetrachloride ($SiCl_4$), hydrogen (H_2) and oxygen (O_2) are reacted with each other to form ultra-fine particles of silicon dioxide (SiO_2) and hydrogen chloride (HCl). Since silicon tetrachloride itself is expensive and the weight ratio of silicon in the silicon tetrachloride is low, the reaction does not suit to the mass production and also results in a problem that noxious by-products such as hydrogen chloride are resulted.

Furthermore, since the production is carried out in an active atmosphere, it is difficult to obtain clean particle surfaces. These problems are also found in other general chemical processes.

The physical process includes, for example, vacuum vapor deposition process, in which moderate evaporizing phenomenon of substance heated to a high temperature under a reduced pressure is utilized. The process is carried out under a reduced pressure in order to facilitate the evaporation of the starting material. This process, however, consumes a great amount of heat energy, as well as provides a problem in that the production speed is slow and, accordingly, does not suit to the mass production.

SUMMARY OF THE INVENTION

Accordingly, it is the primary object of the present invention to provide a process for producing ultra-fine ceramic particles, which can overcome above-mentioned disadvantages.

It is a further object of the present invention to provide a process for producing ultra-fine ceramic particles with high purity.

It is a further object of the present invention to provide a process for producing ultra-fine ceramics, which has an improved heat efficiency.

It is a further object of the present invention to provide a mass productive process for producing ultra-fine ceramic particles.

The foregoing object can be attained in accordance with this invention by a process for producing ultra-fine ceramic particles which comprises the steps of forming powdered dust cloud composed of metal powder constituting a portion of aimed ultra-fine ceramic particles and a reaction gas containing an element constituting the other portion of the aimed ultra-fine ceramic particles, igniting the powdered dust to cause explosive burning and synthesizing the ultra-fine ceramic particles and collecting the ultra-fine ceramic particles.

As the metal for forming a portion of ultra-fine ceramic particles in this invention, silicon, aluminum, titanium, magnesium, iron, zirconium and the like may be used.

The element constituting the other portion of the aimed ultra-fine ceramic particles for use in this invention includes oxygen, nitrogen, carbon and the like; and reaction gases containing these elements include gaseous oxygen, gaseous nitrogen, gaseous ammonium, hydrocarbons or the likes. By varying the types of the reaction gases, oxides, nitrides and carbides or the likes can be obtained.

For producing the ultra-fine ceramic particles, it is desired that the metal powder reacting with the reaction gases is desirably as fine as possible, preferably, of less than 400 μm in particle size. Further, it is desired that the metal powder contains impurities as less as possible.

The metal powder and the reaction gas are rendered into so-called powdered dust cloud upon reaction. It is necessary for the powdered dust cloud that it has a density of more than 20 g/m³, usually, more than 500 g/m³ and, more desirably, more than 1000 g/m³ although depending on the type of the metal powder and the reaction gas. No stable ignition can usually obtained unless the density is more than 500 g/m³.

As the heat source for the ignition, it is possible to use such high density energy source as ohmic heating, arc discharge, plasma flame, laser, high frequency induction heating and electron beams. They are used as the seed fire.

Further a chemical flame containing the gaseous element can be efficiently used both as the heat source and the reaction gas especially for producing ultra-fine oxide particles as the ceramic particles.

Namely, the process for producing ultra-fine oxide particles according to the method in which a chemical flame is used comprises forming a chemical flame containing oxygen, and feeding into the chemical flame metal powder for constituting a portion of aimed ultra-fine oxide particles in such an amount as capable of forming powdered dust cloud, thereby causing explosive burning and synthesizing the ultra-fine oxide particles.

The reaction of this invention can be carried out under an atmospheric pressure. However, it can also be carried out in an elevated or reduced pressure.

In order to obtain ultra-fine ceramic particles by the explosion of powdered dust, the following two conditions have to be satisfied.

(A) There should be a sufficient heat generation to promote the evaporation of metal and cause explosion of powdered dust after ignition. That is, the reaction enthalpy H should be large.

(B) The reaction product (ultra-fine ceramic particles) should be stable at the reaction temperature, that is, the value T obtained by dividing the temperature T_0 ("K.") at the free energy of the product $\Delta G_0 - 0$ with the boiling point T_1 ("K.") of the constituent metal of the product should be large (more than 0.6).

FIG. 1 shows plots for various types of ceramics taking ΔH_0 on the abscissa and T on the ordinate. In FIG. 1, \circ represents ceramics formed by the explosion of powdered dust and \bullet represents ceramics not formed by the explosion of powdered dust, in which constitutional metals with particle size between 200-350 mesh at the concentration of 1000 g/m³ were ignited using reaction gases such as oxygen and nitrogen for investigation.

In FIG. 1, those ceramics situated above the dotted line are obtained by the explosion of powdered dust. As can be seen from FIG. 1, typical ceramics, that is, oxides such as aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), titanium oxide (TiO_2) and zirconium oxide (ZrO_2) and nitrides such as titanium nitride (TiN), and zirconium nitride (ZrN) can be synthesized.

As the method for forming a powdered dust cloud, the following methods can be used.

(1) A reaction gas is at first fitted in a vessel and then a metal powder is injected to be dispersed in the reaction gas. In this case, the metal powder may be injected by a pressurized reaction gas.

(2) A metal powder is set in a vessel and then a reaction gas is injected into the vessel to disperse the metal powder.

(3) A pressurized reaction gas containing a metal powder is injected into a vessel to form a powdered dust cloud.

Also as the method for making a chemical flame, oxygen gas is at first filled in a vessel and then by a burner hydrogen gas is continuously burned in the vessel to form a chemical flame containing oxygen. In stead of hydrogen, hydro-carbon ($CxHy$) or the like can be burned continuously.

These flames are usually formed by using a burner. The use of the chemical flame as the heat source is free from the defects of the method in which a spark discharge is used.

Although the process of utilizing spark discharge for igniting a powdered dust cloud can simplify the structure of the device itself, it has been still somewhat unsatisfactory in that (a) since the high temperature portion forms only a small region, burning can not some time propagate throughout the powdered dust cloud, (b) the burning is only instantaneous and results in only the surface oxidation of the metal powder depending on the case and (c) uniform dispersion of the metal powder is difficult.

Also, the used of the chemical flame can eliminate the following defects in the use of plasma flame;

(a) the initial cost is high due to the facility,

(b) a great amount of gas and electric power are consumed and the life of the electrodes is as short as several hundreds hours, to increase the running cost,

(c) since the plasma flow rate is so high as exceeding the sonic velocity, it is difficult to feed the metal powder therein and a portion thereof is repelled out and remained not burnt, and

(d) since the oxidation is exothermic and caused in a chain-reaction manner, it does not require such high temperature as obtained by the plasma, which means that the heat of plasma is partially spent wastefully.

OPERATION OF THE METHOD IN WHICH A POWDERED DUST CLOUD IS IGNITED

In this method, preferably, a reaction gas is at first filled in a vessel and a metal powder is dispersed in the reaction gas to form a powdered dust cloud at a high concentration (more than 500 g/m³). Then, an adequate ignition source such as arc discharge is actuated and the powdered dust cloud is ignited, whereby heat energy is applied to the surface of the metal powder, the surface temperature of the metal powder is increased and the metal vapor prevails from the surface to the periphery of the metal powder. The metal vapor is mixed with the reaction gas to ignite and produce fire. The heat caused by the fire further promotes the gasification of the metal powder and the metal vapor resulted thereby is mixed with the reaction gas to cause ignition and propagation successively. In this case, the metal powder itself also bursts to scatter and the promote the propagation of the fire. Then, when the resultant gas is cooled spontaneously after the burning, cloud of ultra-fine ceramic particles can be obtained. The ultra-fine ceramic particles thus obtained are collected by being charged in an ordinary electrical dust precipitator or the like.

As described above, the following advantageous effects can be obtained according to the method in which a powdered dust cloud is ignited.

(i) Since the heat generated upon reaction of the vapor of metal powder and reaction gas as the starting material promotes the gasification of further metal powder, necessary heat energy to be applied externally may be such a small amount as capable of producing ignition and the heat efficiency is extremely high (more than 100%).

(ii) Since the principle of the powdered dust explosion is utilized, a great amount of ultra-fine ceramic particles can be obtained instantaneously to provide high mass productivity.

(iii) Since the process according to this invention can be carried out under an atmospheric temperature, the structure of the apparatus can be simplified and the cost can be reduced as compared with the conventional process.

(iv) By increasing the purity of the metal powder and the reaction gas as the starting material, ultra-fine ceramic particles at a high purity and having clean surfaces can be produced.

(v) Since the production step is relatively simple, the process can easily be automated.

OPERATION OF THE METHOD IN WHICH A CHEMICAL FLAME IS USED

In the method, preferably, a gas containing oxygen as the reaction gas is at first filled in a vessel and a hydrogen gas is burned through a burner so that a chemical flame is formed in the reaction gas. Then, metal powder is supplied into the chemical flame to form powdered dust cloud at high density (more than 500 g/m³). Then, heat energy is applied to the surface of the metal powder by the chemical flame, whereby the surface temper-

ature of the metal powder is increased and the vapor of metal prevails from the surface to the periphery of the metal powder. The metal vapor reacts with the oxygen gas to cause ignition and the result in fire. The heat caused by the fire further promotes the gasification of the metal powder, the metal vapor formed thereby and the reaction gas are mixed to cause chain-like ignition and propagation. In this case, the metal powder itself also bursts to scatter and promote the propagation of the fire. Then, when the resultant gas is spontaneously cooled after the combustion, a cloud of ultra-fine oxide particles is formed. The ultra-fine oxide particles thus formed are collected by being charged with an ordinarily electrical dust precipitator or the like.

As described above, according to the method in which a chemical flame is used, the following advantageous effects can be obtained:

(i) since the heat generated upon reaction of the evaporized metal powder and the reaction gas as the starting material promotes the gasification of metal powder in other portions, necessary heat energy applied externally can be such an extremely small amount as capable of causing ignition and the heat efficiency is very much high (more than 100%),

(ii) since the principle of the powdered dust explosion is utilized, a great amount of ultra-fine oxide particles can be obtained instantaneously to provide a high mass productivity,

(iii) since the chemical flame is used as the heat source, mis-firing and incomplete combustion can be prevented to provide completely ultra-fine oxide particles,

(iv) since the metal powder can easily be fed into the chemical flame and the temperature near the exit of the burner is low, no melting and clogging of metal powder are caused as in the case of using the plasma,

(v) since the flow velocity is lower than that of the plasma, the metal powder can stay for a longer time than in the case of the plasma in a high temperature region of the combustible substance forming the chemical flame, and

(vi) since the production step is relatively simple the process can easily be automated.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will now be shown and described with reference to several preferred examples of the method and of the apparatus thereof, and with reference to the illustrative drawings. It should be clearly understood, however, that the description of the preferred examples, and the drawings, are all of them given purely for the purposes of explanation and exemplification only, and are none of them intended to be limitative of the scope of the appended claims. In the drawings, like parts and features are denoted by like reference symbols in the figures thereof, and:

FIG. 1 is a graph showing the result of the investigation for the possibility of forming various kinds of ultra-fine ceramic particles due to the powdered dust explosion;

FIG. 2 is schematic structural view showing the outline of the device for producing ultra-fine ceramic particles employed in the examples according to this invention; and

FIG. 3 is a schematic constitutional view or showing the outline of a device for producing ultra-fine oxide particles employed in the example of this invention.

EXAMPLES

Next, example of this invention will be described referring to the drawing.

EXAMPLE 1

The first example shows a case for producing ultra-fine oxide particles as the ultra-fine ceramic particles.

FIG. 2 is a schematic constitutional view showing the outline of the device for producing ultra-fine ceramic particles used in the first example according to this invention.

In FIG. 2, reference numeral 1 denotes a tightly closed vessel forming an outer casing for the device for producing ultra-fine ceramic particles and a combustion device 2 and a hopper 4 for supplying metal powder 3 are disposed within the tightly closed vessel 1. The combustion device 2 and the hopper 4 are connected by means of a feedpipe 5 and the hopper 4 is further connected with an external reaction gas supply source (not illustrated) by means of a feedpipe 5.

The combustion device 2 comprises a cylindrical portion 2a and a conical portion 2b made of quartz, in which a ball valve 6 made of alumina is inserted to the connection portion between the conical portion 2b and the feedpipe 5. Further, a pair of discharge electrodes 7 are opposed with a predetermined gap at the cylindrical portion 2a of the combustion device 2, and the discharge electrodes 7 are connected to a high voltage transformer 8.

Further, a solenoid valve 9 is disposed at the midway of the feedpipe 5 for connecting the hopper 4 with the combustion device 2, and the solenoid valve 9 is controlled to open and close by a control device 10.

Above the combustion device 2, in the tightly closed vessel, is attached an exhaust pipe 11 and an electrical dust precipitator 12 is mounted at the midway of the exhaust pipe 11. Reference numeral 13 denotes a pressure gage.

Fine oxide particles were produced by using such a ultra-fine ceramic particle producing device.

The metal powder 3 as the starting material was at first charged in the hopper 4. Then, clean air is filled to the inside of the tightly closed vessel 1. Subsequently, the bottom of the hopper 4 is opened and air as the reaction gas from a reaction gas supply source not illustrated is supplied under the pressure of 5 kg/m². In this case, the solenoid valve 9 is closed by the control device 10. While on the other hand, 10 KV (AC) of voltage is applied from the high voltage transformer 8 with the electrode gap between the discharge electrodes 7 being set to 2 mm. As the result, sparks are always generated between the discharge electrodes 7. Under such a condition, the solenoid valve 9 was opened for 0.5 sec. Then, the metal powder 3 was supplied carried on the pressurized air to the conical portion 2b of the combustion device 2, raised the ball valve 6 and formed powdered dust cloud comprising the metal powder 3 while being scattered upwardly to the inside of the combustion device 2. The powdered dust cloud was ignited by the sparks being generated between the discharge electrodes 7 to instantaneously from a combustion flame 14 and, thereafter, spontaneously cooled to form a cloud 15 of the ultra-fine oxide particles. The ultra-fine oxide particles were collected in the electrical dust precipitator 12 and the remaining gases were exhausted through the exhaust pipe 11.

Such ultra-fine oxide particles were produced while varying the materials for the metal powder as shown in the Table 1 below. The ultra-fine oxide particles obtained as the result were observed by a transmission type electron microscope (TEM) to examine the particle size, configuration and crystallinity. The results are also shown in Table 1.

As apparent also from Table 1, it can be seen that ultra-fine oxide particles of sphere or spheric polyhedron with particle size of between 5-100 nm can be obtained by the present example.

EXAMPLE 2

Ultra-fine nitride particles were produced by using the same device as in the first example shown in FIG. 2. The second example was different from the first example in that purified nitrogen gas (99.99%) was introduced up to an atmospheric pressure after evacuating the inside of the tightly closed vessel to more than 10 Torr of vacuum degree, in that an ammonia gas is used as the reaction gas with a gas pressure of 3 kg/cm² and in that the metal powder as the starting material was heated by heating the feedpipe up to 600° C. by ohmic heating, and ultra-fine nitride particles were produced substantially in the same manner as in the first example with respect to other procedures.

Such ultra-fine nitride particles were produced while varying the materials for the metal powder as shown in Table 2 listed below. The ultra-fine nitride particles obtained as the result were observed by a transmission type electron microscope (TEM) to examine the particle size, configuration and crystallinity. The results are also shown in Table 2.

As apparent from Table 2, it can be seen that ultra-fine nitride particles of sphere or spheric polyhedron with particle size of between 5-100 nm could be obtained.

TABLE 1

Synthesized ultra-fine particle	Particle size (nm)	Configuration	Crystallinity	Starting material
Al ₂ O ₃	10-100	Sphere	crystal-line	Al 99.9% less than 200 mesh
MgO	10-100	↑	↑	Mg 98.0% less than 200 mesh
SiO ₂	8-50	↑	amorphous	Si 98.0% less than 150 mesh
TiO ₂	10-100	↑	crystal-line	Ti 99.5% less than 350 mesh
ZrO ₂	10-100	↑	↑	Zr 98.0% less than 350 mesh
Fe ₃ O ₄	5-70	spheric polyhedron	↑	Fe 99.9% less than 200 mesh

TABLE 2

Synthesized ultra-fine particle	Particle size (nm)	Configuration	Crystallinity	Starting material
TiN	10-100	sphere	crystal-line	Ti 99.5% less than 350 mesh
ZrN	↑	↑	↑	Zr 98.0% less than 350 mesh

EXAMPLE 3

FIG. 3 is a schematic structural view showing the outline of a device for producing ultra-fine oxide particles employed in the third example of this invention.

In the drawing, reference numeral 21 denotes a tightly closed vessel forming the outer casing of a device for producing ultra-fine oxide particles, and a gas burner 22 is attached at the bottom of the tightly closed vessel 21. At the top end of the gas burner 22, is mounted a combustion cylinder 23 made of quartz and the top end of an ignition device 24 is attached near the exit of the gas burner 22 in the combustion cylinder 23.

The inside of the gas burner 22 is substantially structured as a double walled pipe, in which the inner space is communicated with one end of an introduction pipe 25. A hopper 26 for supplying metal powder is disposed at the midway of the introduction pipe 25 and a ball valve 27 is disposed to introduction pipe 25 between the hopper 26 and the gas burner 22. The ball valve 27 is controlled to open and close by a control device 28. The introduction pipe 25 is connected at the other end thereof to a hydrogen supply source of the hydrogen is controlled by a valve 29.

To the outer space in the gas burner 22, are opened respective one ends of a first gas pipe 30 and a second gas pipe 31 with the other end of the first gas pipe 30 being connected with an oxygen supply source and the other end of the second gas pipe 31 being connected to a hydrogen supply source. The amount of the respective gases are controlled by means of valves 32 and 33 respectively.

A third gas pipe 34 opens at one end thereof to the inside of the combustion cylinder 23 and communicates at the other end thereof with an argon and oxygen supply source, in which the amount of the gas is controlled by a valve 35.

Further, to an upper portion of the tightly closed vessel 21 situated above the combustion cylinder 23 is attached an exhaust pipe 36, and an electrical dust precipitator 37 is mounted at the midway of the exhaust pipe 36.

Ultra-fine oxide particles were produced by using such a device for producing ultra-fine oxide particles.

At first, metal powder as the starting material is charged in the hopper 26. Then, the valve 35 was opened to introduce a gas mixture of argon and oxygen by way of the third gas pipe 34 to the inside of the tightly closed vessel 21 to replace the atmospheric air therein. The volume ratio between the argon gas and the oxygen was 4:1. Subsequently, valves 32 and 33 were opened to supply oxygen from the first gas pipe 30 at 20 l/min and hydrogen from the second gas pipe 31 at 10 l/min to the gas burner 22, and ignited by the ignition device 24 to form a combustion flame comprising flame comprising an oxygen - hydrogen flame.

Then, the bottom of the hopper 26 was opened and the metal powder was supplied to the gas burner 22 while being carried on the hydrogen at a pressure of 1 kg/cm² by opening the valve 29 while opening and closing the ball valve 27 at 0.5 sec interval by the control device 28. Then, the metal powder scattered upwardly from the exit of the gas burner 22 to form a powdered dust cloud. The powdered dust cloud was ignited by the combustion flame 38 to obtain a great amount of ultra-fine oxide particles through the explosive burning. The cloud 39 of the ultra-fine oxide particles produced through the synthesis was passed to the

electrical dust precipitator 37 to collect the ultra-fine oxide particles.

Such ultra-fine oxide particles were produced while varying the materials for the metal powder as shown in Table 1 listed below. The ultra-fine oxide particles obtained as the result were observed under a transmission type electron microscope (TEM) to examine the particle size and configuration and crystallinity. The results are also shown in Table 3.

As apparent from Table 3, it can be seen that the ultra-fine oxide particles with the particles size of between 5-100 nm can be obtained according to this example, in the shape of sphere or spheric polyhedron.

Furthermore, the rate of synthesis was increased by more than 30% as compared with that produced through the electric discharge ignition as described above.

While this invention has been described with respect to the specific example, this invention is no way limited only thereto but various embodiments are encompassed within the scope of the claim.

For instance, while the process for producing ultra-fine oxide particles and ultra-fine nitride particles have been described in the foregoing examples, this invention can of course be applied to ultra-fine carbide particles.

TABLE 3

Synthesized ultra-fine particle	Particle size (nm)	Configuration	Crystallinity	Starting material
Al ₂ O ₃	10-100	sphere	crystal-line	Al 99.9% less than 200 mesh
MgO	10-100	↑	↑	Mg 98.0% less than 200 mesh
SiO ₂	8-50	↑	amorphous	Si 98.0% less than 150 mesh
TiO ₂	10-100	↑	crystal-line	Ti 99.5% less than 350 mesh
ZrO ₂	10-100	↑	↑	Zr 98.0% less than 350 mesh
Fe ₃ O ₄	5-70	spheric polyhedron	↑	Fe 99.9% less than 200 mesh

What is claimed is:

1. A process for producing ultra-fine ceramic particles which comprises:

- forming a powdered dust cloud composed of metal powder and a reaction gas containing an element for reaction with said metal powder,
- igniting the same to cause explosive burning and synthesizing the ultra-fine ceramic particles, and
- gathering said ultra-fine ceramic particles; and wherein the reaction enthalpy, ΔH_0 , is sufficiently large to generate sufficient heat to evaporate the metal, thereby causing an explosion of the powdered dust after ignition, and wherein the value T, which is the value obtained by dividing the temperature T_0 (°K.) at the free energy of the product ΔG_0 by the boiling point T_1 (°K.) of the constituent metal of the product, is greater than 0.6, indicating that the reaction product is stable at the reaction temperature.

2. The process according to claim 1, wherein the metal forming said metal powder is one selected from the group consisting of silicon, aluminum,

titanium, magnesium, zirconium, iron or a mixture thereof.

- The process according to claim 1, wherein the particle size of said metal powder is less than 400 μ m.
- The process according to claim 1, wherein the density of said metal powder in said powdered dust cloud is more than 20 g/m³.
- The process according to claim 4, wherein the density of said metal powder in said powdered dust cloud is more than 500 g/m³.
- The process according to claim 5, wherein the density of said metal powder in said powdered dust cloud is more than 1000 g/m³.
- The process according to claim 1, wherein said element is one selected from the group consisting of oxygen, nitrogen, and carbon.
- The process according to claim 1, wherein said reaction gas is one selected from the group consisting of gaseous oxygen, gaseous nitrogen, gaseous ammonium, gaseous hydrocarbon or a mixture thereof.
- The process according to claim 1, wherein the step of igniting is carried out by ohmic heating.
- The process according to claim 1, wherein the step of igniting is carried out by arc discharge.
- The process according to claim 1, wherein the step of igniting is carried out by plasma flame.
- The process according to claim 1, wherein the step of igniting is carried out by laser.
- The process according to claim 1, wherein the step of igniting is carried out by high frequency inducting heating.
- A process according to claim 1, wherein the step of igniting is carried out by electron beams.
- The process according to claim 1, wherein said ultra-fine ceramic particles have a particle size of less than 1000 Å.
- The process according to claim 15, wherein said ultra-fine ceramic particles have a particle size of about 10-100 nm.
- A process for producing ultra-fine oxide particles, which comprises:
 - forming a chemical flame containing gaseous oxygen;
 - feeding metal powder into said chemical flame to explosively burn said metal powder and to synthesize the ultra-fine oxide particles; and
 - gathering ultra-fine oxide particles; and wherein the reaction enthalpy, ΔH_0 , is sufficiently large to generate sufficient heat to evaporate the metal, thereby causing an explosion of the powdered dust after ignition, and wherein the value T, which is the value obtained by dividing the temperature T_0 (°K.) at the free energy of the product ΔG_0 by the boiling point T_1 (°K.) of the constituent metal of the product, is greater than 0.6, indicating that the reaction product is stable at the reaction temperature.
- The process according to claim 17, wherein the step of forming a chemical flame comprises filling a vessel with hydrogen and burning the same in said vessel by a burner to form the resulting chemical flame.
- The process according to claim 17, wherein the metal forming said metal powder is one selected from the group consisting of silicon, aluminum, titanium, magnesium, zirconium, iron and the mixture thereof.

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20. The process according to claim 17, wherein the particle size of said metal powder is less than 400 μm .

21. The process according to claim 17, wherein the density of said metal powder in said powdered dust cloud is more than 20 g/m^3 .

22. The process according to claim 21, wherein the density of said metal powder in said powdered dust cloud is more than 500 g/m^3 .

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23. The process according to claim 22, wherein the density of said metal powder in said powdered dust cloud is more than 1000 g/m^3 .

24. The process according to claim 17, wherein said ultra-fine oxide particles have a particles have a particle size of less than 1000 Å.

25. The process according to claim 24, wherein said ultra-fine oxide particles have a particle size of about 10-100 nm.

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